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AeroVironment, Inc, Pasadena, Ca

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Evaluation of Measurement Approaches

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This report evaluates five techniques for measuring the transport of ozone and precursors into an urban area. These techniques were tested in Philadelphia during the summer of 1978. The data collected in the field program indicate that, in general, advection of ozone aloft is the main route by which pollution of photochemical interest is transported into Philadelphia. Transport of ozone along the surface and transport of oxides of nitrogen and non-methane hydrocarbons, both aloft and along the surface, are minimal. Thus, the recommended techniques must primarily be able to quantify the ozone transported aloft. Of the five techniques, three were determined applicable for quantifying the ozone transported aloft. These three techniques are: (1) fixed surface monitoring upwind; (2) a dedicated instrumented aircraft; and (3) a free lift balloon ozonesonde system. The selection of one of these techniques by an air pollution control agency would depend on the agency's technical expertise, funding available, and the intended use of the data.

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ABSTRACT

This report evaluates five techniques for measuring the transport of ozone and precursors into an urban area. These techniques were tested in Philadelphia during the summer of 1978. The data collected in the field program indicate that, in general, advection of ozone aloft is the main route by which pollution of photochemical interest is transported into Philadelphia. Transport of ozone along the surface and transport of oxides of nitrogen and non-methane hydrocarbons, both aloft and along the surface, are minimal. Thus, the recommended techniques must primarily be able to quantify the ozone transported aloft. Of the five techniques, three were determined applicable for quantifying the ozone transported aloft. These three techniques are: (1) fixed surface monitoring upwind; (2) a dedicated instrumented aircraft; and (3) a free lift balloon ozonesonde system. The selection of one of these techniques by an air pollution control agency would depend on the agency's technical expertise, funding available, and the intended use of the data.

EXECUTIVE SUMMARY

The objective of this study was to evaluate and demonstrate approaches for measuring the transport of ozone and precursors into an urban area. To achieve this objective, five measurement techniques were tested in Philadelphia during the summer of 1978. These five approaches were:

1. Surface measurements at fixed sites;
2. Airborne measurements by dedicated instrumented aircraft;
3. Airborne measurements by a portable instrument package in a light aircraft;
4. Soundings by ozonesonde beneath a free lift balloon; and
5. Soundings by ozonesonde beneath a tethered balloon.

From the data collected by these various techniques we obtained certain useful information on the transport of ozone and precursors into Philadelphia, including:

1. From the fixed sites located upwind for this study, only minimal transport of ozone, oxides of nitrogen, or non-methane hydrocarbons was observed along the surface into Philadelphia during the early morning hours.
2. Transport of oxides of nitrogen and non-methane hydrocarbons aloft is slight.
3. Transport of ozone aloft, in excess of .08 ppm, was sometimes observed during transport days.

4. There is no significant difference in ozone concentrations laterally along the upwind boundary of Philadelphia in the air mass aloft. Differences have been observed at surface stations, probably due to variabilities in the strengths of ozone scavengers, and in the strengths of sources of precursors in the vicinity of the monitoring stations.

5. Trajectories on photochemically active days with strong transport* indicate that the incoming air mass generally approaches Philadelphia from the west in a broad, anticyclonically curved path and does not routinely traverse any particular urban area upwind.

Of the five measurement techniques evaluated, surface measurements at fixed sites, airborne measurements by dedicated instrumented aircraft, and soundings by ozonesonde beneath a free lift balloon are all viable means of measuring directly or providing useful information on ozone concentrations aloft.

An air pollution control agency, in selecting the technique to use, should consider factors such as its technical capability, funding available, and the intended use of the data. The table on the following page ranks the three acceptable approaches in terms of cost, technical expertise required to operate, and the uses of the data generated, and serves to guide the agencies in making the selection.

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*criteria for such days are given on pp. 63-64.

EVALUATION OF PROVEN APPROACHES FOR MEASURING OR OBTAINING INFORMATION ON OZONE CONCENTRATIONS ALOFT.

Method	Approximate Costs			Technical Expertise Required	Intended Use of Data		
	Initial Cost	Operation			Routine Surveil-lance	Input to Models	Vertical Profiles
		Labor[a]	Other				
1. Surface Measurements at a Fixed Site	$30,000[b]	$16,000/month	$500/month	Moderate	X	X	X
2. Airborne Measurements, Dedicated Aircraft	$70,000[b]	$160/flight	$250/flight	High		X	X
3. Soundings, Ozonesonde underneath Balloon	$ 5,000	$80/sounding	$250/sounding	Low		X	X

[a] Labor rate assumed to be $8/hour.

[b] Cost applies to the measurement of ozone only. Additional costs will be required for measuring the parameters.

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Mr. Don Gonzales, Data Processing
Dr. Andrew Huang, Quality Assurance
Mr. Martin Ledwitz, Data Analysis
Mr. David Pankratz, Field Operations
Ms. Diane Barker, Report Editing
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Ms. Gloria Best, Technical Illustrating

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1. INTRODUCTION

The transport of ozone and its precursors has been reported by many investigators. Evidence of the transport of oxidants from urban to rural locations has been reported for the Washington, D.C. area (Wanta, et al, 1961), New Jersey (Leone, et al, 1968), Staten Island and the Bronx (Scott Research Labs, 1970), and Santa Ynez Valley in California (Baboolal, et al, 1975). Long-range transport of ozone and its precursors by air masses is indicated by data obtained in the Los Angeles Basin (Edinger, et al, 1972; Stephens, 1977), the Washington-Baltimore area (U.S. EPA, 1973), Southern Ontario (Yap and Chung, 1977), Wisconsin (Lyons and Cole, 1976), and Connecticut (Wolff, et al, 1977). The ozone laden plume from St. Louis was tracked out to 240 km and was mapped in detail out to 160 km by White, et al (1976). Cleveland, et al (1976) demonstrated by statistical analysis that ozone was transported over 300 km from New York to northeastern Massachusetts.

These and other studies have demonstrated that ozone and precursors can be transported over long distances. Control strategies designed for attainment of the ozone standard in individual urban areas must take into consideration the impact of transported ozone and precursors. The effectiveness of possible control strategies is usually determined through mathematical modeling. Unfortunately, there has generally been a lack of monitoring upwind of urban areas to assess the transport of ozone and precursors. Thus, the impact of such transport on the maximum ozone concentration downwind of an urban area is difficult to assess and cannot be properly modeled.

Even though it is obvious that measurements should be made to quantify the transport of ozone and precusors, there is a general lack of information on when, where, how, and how much upwind monitoring data are needed to determine the contribution of the transported ozone and precursors to the downwind ozone maxima.

In order that states can design control strategies to attain and/or maintain the ozone standard in individual urban areas that are affected by transported ozone and precursors, guidelines have to be established by EPA on techniques to measure the transport.

As a step toward developing guidelines for quantifying the impact of transported ozone and precursors on maximum ozone levels in an individual urban area, AeroVironment was selected by EPA to evaluate a number of techniques for measuring such transport. Those techniques were evaluated during a field program conducted in the summer of 1978 in the vicinity of Philadelphia, Pennsylvania. The specific question of the effect of transported pollutants on the maximum ozone reading in an urban area was not the primary concern of this study. Other studies are planned by EPA to fully address that issue.

This report describes the operation and findings of the field program conducted by AeroVironment and presents an evaluation of the various measurement techniques tested in the field.

2. REVIEW OF METHODS FOR MEASURING OZONE AND PRECURSOR TRANSPORT

The two primary mechanisms by which ozone and precursors might be transported into an urban area are:

Advection of polluted air (ozone and/or precursors) along the surface, and

Advection of polluted air aloft, typically at night and during early morning hours above the ground-based inversion, with downward mixing when the inversion dissipates later in the day.

Overnight advection of ozone and precursors aloft appears to be the more significant mechanism of transport from one urban area to another. Chapter 5 contains a detailed discussion of transport mechanisms.

To determine the degree of ozone and precursor transport, therefore, we must measure wind speed and direction and the concentrations of ozone, NO/NO_2, and non-methane hydrocarbons at the height of the major portion of the transport flux. In general, this implies that at least some measurements will have to be made aloft, some hundreds of meters or more above the surface.

2.1 DISCUSSION OF MEASUREMENT TECHNIQUES

There are a number of specific ways by which we can measure the transport phenomenon, and we have selected nine such methods for review here. All of them are reasonably feasible within the range of financial and technical capabilities of state and local air pollution control agencies. This is a basic requirement of any measurement technique to be developed since state and local agencies are responsible for identifying ozone problems in the urban areas within their jurisdiction and for developing control plans to attain the ozone standard. These nine methods are:

- Method A: Surface measurements at fixed sites.
- Method B: Surface measurements by moving vehicle.
- Method C: Measurements on tall towers.
- Method D: Airborne measurements by dedicated instrumented aircraft.
- Method E: Airborne measurements by a portable instrument package in a light airplane.
- Method F: Airborne measurements by an instrumented manned balloon.
- Method G: Soundings by instrument package beneath a free lift balloon.
- Method H: Soundings and airborne measurements by tethered balloon.
- Method I: Remote sensing of conditions aloft by sensors on the surface.

This list may not be all-inclusive, but it should represent all the economically feasible methods within the state-of-the-art at this time. Remote sensing from aircraft and satellite have definite appeal, but are not yet available for routine use. Obviously, two or more methods can be combined in one study to form the most effective approach to data gathering for any given area. Each method will be discussed separately below.

2.1.1 Method A: Surface Measurements, Fixed Sites

The traditional method for defining pollutant concentrations and transport utilizes a network of fixed stations, each equipped with sensors for the pollutants of interest and some with a wind vane and anemometer to define the direction and speed of surface airflow. Since most urban areas already have such stations, their use for this purpose has obvious economic appeal.

In reality, however, existing ozone and precursor measurement sites are generally located within the urban area and downwind of it, in the area of impact, and seldom does one find a suitably located station upwind. Consequently, an additional fixed site (or sites) might be needed upwind of the city to measure the O_3, NO/NO_2, and hydrocarbon concentrations which are transported into the urban area.

No surface-based network will be able to assess transport aloft when a surface-based inversion isolates conditions aloft from surface reactions. The surface wind direction will generally differ by about 45^o from the wind direction aloft in relatively flat areas, with larger deviations possible near mountains. If desired, pilot balloon tracking measurements, by theodolite, can provide data on winds aloft on days without low clouds. Also, Doppler acoustic radar is now available for determination of winds aloft up to one kilometer above the surface. As will be pointed out in Chapter 5 of this report, a simple non-Doppler acoustic radar can be an indispensable addition to a surface air quality station, allowing inferences of upper air ozone transport using surface O_3 measurements.

Surface stations have the advantages of space and power availability and thus can measure several parameters of interest. Even on-site hydrocarbon speciation analyses can be done for individual hydrocarbons by automated gas chromatography. Since the stations are fixed, however, several might be necessary to adequately define the spatial variability of the upwind air mass.

If existing monitoring networks can be used for measuring incoming transport, then the surface-based approach has very low incremental costs. On the other hand, furnishing and installing a new station for O_3, NO/NO_2, non-methane hydrocarbon, and wind measurements costs from $40,000 to $60,000. Monthly operation and data processing costs will typically amount to $2,000 to $5,000, depending upon the degree of station automation.

2.1.2 Method B: Surface Measurements, Moving Vehicle

A versatile form of surface-based monitoring involves an instrumented vehicle which is totally self-contained and is able to monitor pollution and meteorology while moving or stopped for brief periods. The moving vehicle suffers from the lack of ability to measure conditions aloft, much the same as the fixed stations do, but offers appealing advantages in flexibility. Such a vehicle can follow an air mass as it travels from upwind areas into the city, and can also measure profiles transverse to the wind to determine the spatial inhomogeneity of the arriving air mass. By its motion, however, the moving station loses the ability to observe temporal variability of conditions at a point, although repeated surveys over a fixed route of travel can provide both a temporal and spatial picture.

Moving stations of this type are currently being operated by the EPA, several air pollution control agencies, and many environmental consulting firms. They range in sophistication from commercially available moving laboratories equipped with computerized navigation systems monitoring the vehicle location and correlating it with the pollutant data, to simple vans with a few air quality analyzers and strip chart recorders either temporarily or permanently installed.

Electrical power for operation while moving can be provided by a battery-inverter arrangement or by a small propane-fueled generator; or battery-operated equipment can be used. When the vehicle is stopped for a few hours or more, electricity must be generated by the vehicle generators or an auxiliary generator. In all cases, the available electrical power is limited, and cooling or heating of the operating environment to assure proper instrument operation must be provided by the vehicle's own environmental control systems. In addition, exhaust from the vehicle engine or a generator can pose vexing sample contamination problems when the vehicle is stopped.

Vehicle engine exhaust can also affect the instrument measurements while moving, for two reasons. First, because of a possible recirculating airflow around the truck or van, exhaust from the engine could contaminate the air samples. Careful testing of the actual installation (or a wind tunnel model) is necessary to insure that this does not occur. Second, the exhaust emissions from other vehicles will result in higher NO/NO_2 and hydrocarbon levels and lower O_3 levels on the roadway than in the surrounding area. Consequently, moving laboratory measurements made in heavy traffic will not be representative of the oxidant and precursor levels for that location.

Reliable wind measurements are difficult to make from a moving vehicle and require sophisticated sensors of vehicle motion. Thus, it is generally preferable to make wind measurements when the vehicle is stopped for brief periods. Proper wind instrument exposure is also a problem since tall masts cannot be mounted on moving vehicles; telescoping masts can be used to support instruments when the vehicle is stopped, however.

A typical dedicated moving vehicle will cost from $75,000 to more than $150,000, with monthly operating and data processing costs varying from about $5,000 to $15,000, depending upon the degree of automation of the data collection equipment on board. It costs more initially than a fixed station because of the vehicle itself, the electrical power generation equipment, and the more difficult installation and monitoring requirements for instrumentation to be used while moving. Data processing costs are higher because when the vehicle is used in a moving mode the position of the vehicle is a continuously changing parameter.

To provide the flexibility of moving measurements at lower cost, simpler, ad hoc arrangements of instruments in an available motor-home or van will often suffice for a few days of measurement. However, a proper operating temperature and provision of sufficient electricity for environmental control and instrument operation generally requires a dedicated vehicle.

2.1.3 Method C: Tower Measurements

The depth of the nocturnal surface-based inversion which isolates pollutants aloft from surface emissions is often fairly shallow -- from tens of meters to a few hundred meters. Also, the major portion of the turning of the wind vector between the surface and aloft occurs in the first few hundred meters above the ground. Consequently, a sensor situated 100 meters or more (preferably more) above the surface will often describe conditions within the inversion or even above it, or will at least provide a basis for estimating these conditions.

Such a height is achievable by installing air quality and meteorological sensors on existing radio/TV towers or on tall buildings. In effect, a fixed air monitoring station, such as in Method A, can be installed on an elevated platform. Obviously, such an approach will work only if an existing tower or building is in the proper location, since the cost of constructing a tower specifically for this purpose is formidable.

An installation on a tall building, especially on the roof, is relatively straightforward, although care has to be taken to locate air quality sample inlets away from building air exhaust ducts, and the effect of the airflow around the building on the anemometer has to be considered.

Installations on tall towers can be complex, especially since the sample lines to air quality analyzers should be no longer than a few meters. Maintenance of instruments installed on towers can be difficult. Also, the strength of the radio frequency radiation field around broadcasting towers can interfere with the proper operation of the electronic portions of analyzers and recorders unless proper, and sometimes elaborate, shielding techniques are used. (In some instances, adequate shielding will be impossible and the site will be unsuitable for some of the instruments.) Sometimes, the wind load structural limits of the tower will preclude major equipment installation on the tower itself, so that only a few sensors or sampling devices can be mounted on it, and the bulk of the signal processing electronics will have to be located at the tower base.

In spite of these limitations and difficulties, when a tower exists in the proper location installation of an air quality and meteorological station on it may be an effective approach to the acquisition of pollutant transport data. To supplement the main measurements, carefully matched temperature sensors should also be installed at several locations on the tower to define the lapse rate profile and locate the inversion level, thereby identifying the air mass which is being monitored. A standard ground-based air quality station should be located near the tower to provide a complete picture of the pollutant transport situation.

An excellent example of an instrumentation installation on a tower is provided by the Mt. Sutro television tower near San Francisco (DeHay, 1974; Russell and Uthe, 1976). The Mt. Sutro system has been used to study the vertical structure of ozone concentration, and its relation to the meteorological situation (MacKay, 1977).

Although this tower is comprehensively instrumented for detailed boundary layer research and, therefore, contains many sensors which would be of no interest for oxidant transport investigations of concern here, the design of the system is worthy of review by anyone intending to install a monitoring station on another tower.

A simple installation in a tall building will cost at least as much as the $50,000 to $100,000 range of a fixed-surface site; the cost of an installation on a tower can be significantly greater depending on the constraints imposed by the tower design and use. Operating costs start at the same $2,000 to $5,000 range as for a fixed surface site and extend upward depending on the difficulty of access to the instruments for maintenance.

2.1.4 Method D: Airborne Measurements, Dedicated Instrumented Aircraft

In the past five years, the use of instrumented aircraft for air pollution surveys has become rather commonplace. Aircraft offer advantages of both horizontal and vertical mobility, and can map out the characteristics of large volumes of air in a short period of time. Example of studies in which instrumented aircraft have been used to study urban air quality include measurement programs in Los Angeles and San Francisco (Blumenthal, et al, 1974) and in Denver (Anderson, et al, 1977).

The most effective approach to aircraft measurements involves an aircraft in which instrumentation has been installed in a relatively fixed manner, appropriate connections and modifications have been made to the aircraft electrical system to power the equipment, and properly designed sampling probes have been inserted into the airstream. Aircraft space, weight-carrying capacity, and electric power are generally limited, and such installations therefore require careful design to satisfy these limitations.

The sampling probe location must be chosen to avoid sampling the engine exhaust. For twin-engine aircraft a probe in the nose or on top of the forward part of the fuselage is generally satisfactory, while for a single-engine aircraft a location on the wing (for high-wing models) or on the upper part of the fuselage has been found to be adequate (Adams and Koppe, 1969). Helicopter sampling probe locations depend greatly on the helicopter configuration; generally a probe as far forward as possible, and as low as possible, provides the most representative sample. For the gaseous pollutants of concern here, isokinetic sampling is not necessary, but, as with fixed stations, the residence time of the sample in the sampling system should be as brief as possible.

Because such an installation results in modifications to the aircraft structure and systems, the Federal Aviation Administration (FAA) requires relicensing of the aircraft in a "restricted" category -- a relatively straightforward process for an aircraft mechanic who has experience with special-use aircraft modifications. The fixed installation can also include connection of the aircraft navigational and operational instruments to a recorder so that the air quality and meteorological data collected can be correlated with the location of the aircraft.

A typical aircraft flight path for profiling the air mass might look like the representation in Figure 1. The path consists of spiral soundings to define the vertical structure and horizontal traverses to define the spatial distribution. Because of the high speed of the aircraft, any given area can be repeatedly surveyed at frequent intervals, thereby providing a fairly continuous picture of the situation at any given location. If the soundings can be made near the ground, as at airports or in open areas, the aircraft can provide measurements representative of surface conditions. In general, though, operations below 150 m above the surface are not permitted, and even flying at that altitude over populated areas requires special authorization from the FAA.

Aircraft measurements are limited to relatively fair weather conditions, since the ability of an aircraft to fly patterns which do not conform to normal air traffic flow is severely limited by air traffic control procedures whenever significant clouds are present in the flight area or the visibility decreases below 5 kilometers. Also, operations in the vicinity of major air terminals are difficult because of the inconvenience they can cause other aircraft.

An instrument system installed in an aircraft can be used to measure O_3, NO/NO_2, and total hydrocarbons. Total hydrocarbons can be measured by continuous

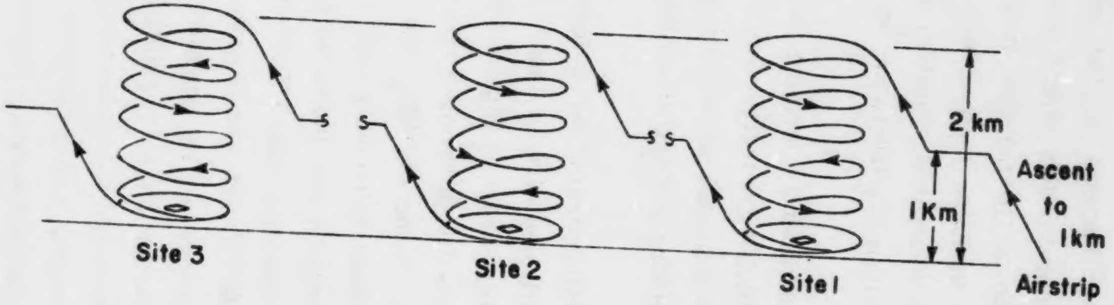
2 km
1Km
Ascent to 1km
Airstrip
Site 1
Site 2
Site 3
S
S

FIGURE 1. Typical flight pattern for aircraft surveys.

flame ionization detectors; the gas chromatographic analyses needed for non-methane hydrocarbon (NMHC) measurement, or for further speciation of hydrocarbons, are generally not done in aircraft because of the low sampling frequency of gas chromatographs (once per 5 minutes or less often). Continuous NMHC measurements, such as by catalytic conversion of the methane in the stream, are not yet reliably achievable. Hence, the only workable method for airborne NMHC measurements involves sample collection in evacuated canisters or flow-through glass sampling containers, with subsequent analysis in a laboratory on the ground.

Aircraft also cannot conveniently measure winds aloft, at least not without expenditure of the order of $100,000 for inertial or Doppler navigation systems. Thus, determinations of air pollutant transport will require supporting wind measurements by surface-based pilot balloon tracking or Doppler acoustic radar.

To resolve the spatial distribution of air pollutant concentrations from a moving aircraft requires that the instrumentation on board have a faster response to changes in pollutant concentrations than would be required for measurements at a fixed site. The performance specifications for automated reference and equivalent methods in 40 CFR53.20 require that, for ozone and NO_2, the instrument lag times be no more than 20 minutes and the rise times be no more than 15 minutes. For spatial resolution of, say, two kilometers horizontally and 100 m vertically, and with instruments in an aircraft traveling at 50 m/s (approximately 100 knots) and ascending or descending at 150 m/min (approximately 500 ft/min), the response time of the instruments would have to be 40 seconds, however. The commercially available O_3 and NO/NO_x analyzers which are of interest for aircraft applications and which have received EPA designation, do have response times considerably faster than those required by 40CFR53.20, but they do not have a response time of better than 40 seconds. Faster response times are available on most instruments, usually by changing a switch setting, but the EPA designation no longer applies when the instrument is operating in this faster mode. This presents a dilemma, since monitoring instruments used in support of a State Implementation Plan must be designated by EPA in accordance with 40CFR53, but use of such currently available instruments in aircraft would not, in general, provide data with the spatial resolution needed for effective use of the data. Thus, at the moment, all air pollution research aircraft known to us (including the EPA helicopter used in this study) use instruments which are not in compliance with 40CFR53 because their control settings do not conform to those which are required for operation as a designated method. Obviously, if aircraft are going to be used routinely for control strategy development purposes, it will be necessary for instrument manufacturers to achieve the specifications of 40CFR53 with much faster response times or for the EPA to recognize the special nature of aircraft measurements and, therefore, to adjust 40CFR53 to allow otherwise acceptable currently available instruments to be used on faster response scales with some attendant degradation in instrument signal quality.

A major drawback to the use of dedicated aircraft is the initial cost, with the aircraft itself a major component of the cost. A new light, single-engine aircraft suitable for installation of a minimal ozone profiling measurement system (O_3, temperature, altitude, recorder) will cost in the vicinity of $50,000; prices for a new twin-engine aircraft suitable for a more sophisticated installation with NO/NO_x and navigational data recording added, and with room for hydrocarbon sampling containers, begin at $150,000. Consequently, the total cost of a dedicated aircraft will be a minimum of about $70,000 for a simple installation in a single-engine light plane, and can easily reach $200,000 or more if twin-engine aircraft and sophisticated recording systems are desired. The operating cost, which will range from $100 to $500 per flight hour for light aircraft, including crew but excluding post-flight data processing, can be very reasonable in terms of the amount of data collected. Data processing costs will vary widely, depending on the number of parameters recorded, the type of flight profile, and the type of the data logging systems on the aircraft. Thus, the data processing cost can range from $50 to $200 or more per flight hour.

2.1.5 Method E: Airborne Measurements, Portable Instrument Package

As was mentioned above, airplanes offer an effective platform for airborne soundings of air pollution and temperature. The major stumbling block to their use is the cost of instrumenting and maintaining a dedicated aircraft. On the other hand, ad hoc instrument installations in aircraft tend to be difficult because of requirements for electric power, carrying of compressed gas, and electrical and radio frequency noise and interference. Any electrical connection to an aircraft requires recertification of the airplane into a "restricted" category. The effect of carrying compressed or flammable gases (ethylene, for example) is the same. Thus, a simple installation of standard air quality instruments for short-term studies using a rented airplane is generally not possible.

The availability of new, flyable, battery-operated O_3 and NO/NO_x analyzers* offers a new approach to airborne measurements. These analyzers, plus battery-operated recorders, can be installed in small cases which can be strapped down onto the seats of an aircraft. A thermistor temperature sensor can be included to record the air temperature, and an event mark button can be clipped to the aircraft control wheel and used by the pilot for marking cardinal events (for instance, crossing of selected altitudes or passage of significant landmarks) on the chart records.

Samples can be carried to the analyzers by a 1- to 2-cm diameter Teflon line threaded through the cabin fresh air inlet of the aircraft and extended out into the free airstream. The airflow through the sample line is ram air-driven. Only a small portion of the flow is needed by the analyzers; the rest can be released into the cabin or used for hydrocarbon grab sampling. The temperature sensor can also be installed in the same fresh air vent as the sample tube.

Such a system offers many of the advantages of dedicated aircraft and, in addition, is inexpensive to operate -- no installation is required -- so any rented or chartered small aircraft (such as a Cessna 172 or a Piper Cherokee) can be used; the only cost is for the aircraft and pilot during the actual time flown. The portable instrument package may be able to be flown closer to the ground than systems in larger aircraft simply because of less aircraft noise. It can also be used in a helicopter. The measurement system is simple enough that, for repeated measurements, the pilot can operate it alone and an observer is not needed. When there is extensive air traffic, however, the pilot alone may be fully occupied with flying the aircraft and may not be able to monitor whether the instruments are operating properly.

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*manufactured by Columbia Scientific Instruments, Austin, Texas, (O_3 and NO/NO_x) and Analytical Instrument Development, Avondale, Pennsylvania (O_3 only).

Because the currently-available portable O_3 analyzers require compressed ethylene gas for operation, use of such an analyzer in a normal light plane is not permitted without special arrangements, however. Two options are possible: (1) certification of the aircraft in the "restricted" category whenever the analyzer is being operated on board, or (2) obtaining of an exemption from the Department of Transportation regulations covering the carriage of hazardous materials in an aircraft, following 41CFR107.101. The former approach is easy to implement and places no limitations on use of the aircraft when the analyzer is on board. It may require additional insurance coverage by the aircraft owner, however. The second approach, to our knowledge has not yet been tried for this purpose; it will probably present the same insurance situation. A third approach for using the O_3 analyzer legally, which was tried during this study, is to use non-flammable Ethychem gas (a mixture of CO_2 and C_2H_4) instead of pure ethylene. As will be discussed in Section 5.3, this approach was not totally successful because the instrument sensitivity was reduced when the Ethychem was used.

Other disadvantages of the portable system are much the same as for the dedicated aircraft system. In particular, hydrocarbon measurements can be done only by grab sampling, in much the same way as for the dedicated aircraft. Also, experience with such portable systems in aircraft is still limited. Unless the manufacturer can provide data on the variation of instrument calibration with altitude, the user will have to perform such calibration tests himself.

An additional disadvantage of the portable instrument package approach, when compared to a dedicated aircraft, is the lack of precise position data for the aircraft. All coding of aircraft position is provided by noting altitude and location on a log and marking the corresponding point on the concentration strip chart with the event marker. Thus, the aircraft position is recorded at discrete intervals and not continuously. This becomes a disadvantage when the visibility is poor in areas with few landmarks to define location or whenever the pilot workload is heavy because of air traffic control procedures, other aircraft in the area, or a complex flight pattern; in such cases, the intervals between logged event marks might be greater than desirable.

A portable instrument package which records O_3 and temperature will cost about \$8,000; one which also records NO/NO_x costs about \$16,000. Rental of an appropriate aircraft with pilot costs \$40 to \$50 per hour. Data processing costs would vary with the type of profiles flown; our experience with the package tested in this study indicates a range of \$75 to \$100 per hour of data collected.

2.1.6 Method F: Airborne Measurements, Manned Balloon

In the last few years, instrumented manned balloons have been used to study urban air pollution in the area of Los Angeles (Heinsheimer, 1977) and St. Louis (the DaVinci II experiment; Environmental Science and Technology, 1976, and Forrest, et al, 1979). Since a balloon is a quasi-Lagrangian tracer of air mass motion, it can follow the progress of photochemical reactions in an air mass as it approaches an urban area and passes over it.

Manned balloons are expensive to purchase, difficult to use (require large ground crews for launch and recovery) and have no on board electrical capability. Nevertheless, their ability to study a specific air mass for long periods (even days) has appeal for research purposes. Because of their operational disadvantages, however, it is unlikely that manned balloons would be used routinely by most air pollution control agencies for assessing pollutant transport at urban areas for purposes of control strategy development. Consequently, a detailed analysis of this approach will not be carried out here.

2.1.7 Method G: Free Lift Balloon Soundings

Free balloons are used routinely for ozone soundings of the troposphere and stratosphere, and for measuring atmospheric temperature, relative humidity, and winds aloft. The use of free balloons for ozone soundings of the polluted mixed layer near the surface appears to be a straightforward combination of these well developed techniques.

The measurement system consists of a iodometric electrochemical ozone sensor which was designed for use with a radiosonde. For use in this study the ozone sensor* was combined with a minisonde** containing a radio transmitter to telemeter measurements of temperature, pressure, and ozone to a ground receiver.

The combined ozonesonde/minisonde instrument package is flown under a free 350-gram balloon with a rate of rise of approximately 100 m/min. The temperature and pressure information transmitted by the package allows calculation of the balloon altitude, by integration of the barostatic equation; the ozone and temperature information records then provide profiles of ozone and atmospheric stability with altitude.

This measurement system provides information on inversion heights and ozone layers aloft but it does not measure precursors. It would normally be launched near an existing air monitoring station, which would thus give ground values of ozone and, possibly, NO/NO_x and hydrocarbons. Winds aloft can also be obtained by tracking the balloon with a theodolite, as long as the balloon is clear of clouds.

This package is lost after each flight. Each package could be equipped with a parachute and tagged with a label offering a reward (say, $25) for its return, but experience suggests only a relatively small fraction of these packages would be returned. Those that are returned can be refurbished and reused.

The performance characteristics of the electrochemical ozone sensor were studied by Torres and Bardy (1978). The ozone sensors measure total oxidants and thus also respond to SO_2 (100% negative interference) and, to a lesser degree, NO_2 (10-20% positive interference). These pollutants are of no concern for the stratospheric measurements for which the ozonesonde was designed, but can severely impair the effectiveness of the method in the polluted air of the boundary layer. Removal of SO_2 and NO_2 from air streams, with negligible effect on O_3 concentrations, has been

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*manufactured by Mast Development Corporation, Davenport, Iowa
**manufactured by Atmospheric Instrumentation Research, Boulder, Colorado

achieved using an absorber column packed with silica gel soaked in sodium dichromate and sulfuric acid and then dried. The method is described by Saltzman and Wartburg (1965) and an application of a variant of the technique is described by Miller, Wilson and Kling (1971).

The major virtues of this approach are:

- simplicity – only one technician is needed
- flexibility – it can be used anywhere (even near airports, with FAA concurrence, and in the center of an urban area) and will work in fog and clouds
- mobility – successive soundings can be performed at different locations as rapidly as one can drive from one to the next
- rapid response deployment – can be used on short notice since no installations are required

The primary disadvantage of the approach is its lack of precursor measurement capability -- it measures only oxidants. It does, however, provide this data continuously from the surface upward and in conjunction with simultaneous lapse rate data and wind data, if desired.

The purchase price of the ground radio equipment and recorders is about $5,000; a theodolite adds about $4,000. The cost of each launch is about $250 for the instrument package and materials. Labor costs for the launch and data reduction will be about $80 if the balloon is not tracked by theodolite, and about $120 if the wind information is obtained.

2.1.8 Method H: Soundings by Tethered Balloon

The instrument package of Method G can equally well be suspended beneath a tethered balloon, which enhances the overall utility of the ozone sounding package. When supported by a small tethered kite balloon (kytoon) the instrument package is retrieved after each flight and can be reused.

A 4.25 m^3 balloon is large enough to lift the instrument package but can still be handled by one technician in calm conditions, and by two technicians in moderate (10 m/s) winds. The balloon is small enough to be stored in a single-car garage overnight so that daily deflating and refilling with helium is not necessary. A commercially-available kytoon sounding system* uses a sensor package which also records winds, and which can be mated to the ozonesonde.

The tethered ozone and temperature sounding package will generally provide atmospheric lapse rate and ozone data to a maximum height of about one kilometer --in the same manner as the system in Method G. The maximum height would be less in strong winds (> 10 m/s) and also at high altitudes (such as Denver) where the lift of the balloon is less.

Most of the advantages and disadvantages of the free balloon system also apply to the tethered system, with the following differences:

- Soundings can be made repeatedly with the same package.
- The tethered balloon system can be "parked" at a given altitude to monitor the temporal variability of ozone aloft at a fixed location.
- The tethered system cannot be used near airports because the tether lines make it a hazard to aircraft.
- The kytoon is clumsy to move and handle in comparison to the small free balloon.

The efficiency of the NO_2/SO_2 scrubber, which was discussed for use with the free balloon method, degrades (for NO_2 removal) as the scrubber is exposed to humidity for extended periods. Because the tethered system can be flown for extended periods, a different technique for the removal of the interferents may be needed. A technique using CrO_3 and H_2SO_4 impregnated filter paper to remove SO_2 has been discussed by Saltzman and Wartburg (1965), as well as in Methods of Air Sampling and Analysis (1972, American Public Health Association). This technique has the disadvantage that it converts NO to NO_2 and, therefore, increases the concentration of that interferent; but it would be useful when NO and NO_2 levels are low and thus the total NO_x effect negligible.

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*manufactured by Atmospheric Instrumentation Research, Inc., Boulder, Colorado

The cost of the kytoon system with the ground-based receiver and recorder is about $10,000. Daily operating costs are primarily for the labor and should be less than $500, while data processing costs depend on the level of detail which is sought. The same ground receiver is usable with the instrument packages for both the free and tethered balloon systems.

2.1.9 Method I: Remote Sensing

All the methods discussed above for the sensing of wind or air pollution aloft are relatively cumbersome to use. The ideal method would involve continuous ground-based sensors which could measure pollutant and wind data aloft. Some of these sensors already exist, and a few are even commercially available or soon will be. Therefore, reality may not be too far from the ideal, at least for some parameters.

The most developed method for the measurement of pollutant concentrations aloft is correlation spectroscopy (Millan and Hoff, 1978). Here, the spectrum of light originating from a source (generally, the sun) and passing through the air mass is compared against the spectral absorption characteristics of NO_2 to determine the total amount of NO_2 along the light path. Since most of the NO_2 is near the earth, in the mixed layer, this allows calculation of the average concentration of NO_2 within that layer; it cannot, however, provide information on the vertical distribution of NO_2. The data obtained, when combined with a mean wind derived from other measurements, allows calculation of the total flux of NO_2 which is being transported by the wind. The method has also been used for SO_2, but not for O_3 or hydrocarbons.

Active remote sensing techniques using a laser light source and observing scattered or re-emitted radiation from the illuminated portion of the air mass are currently being tested. These laser techniques are able to measure pollutant concentrations in a well-defined remote volume, and thus can measure spatial distributions. Because of signal strength requirements, their greatest success is likely to be in the area of measurement of smokestack plumes, but some ambient measurements may also be possible. Remote measurements of ambient O_3 and other pollutants have been made over a closed path, but such methods are not useful for measurement of pollutants aloft. At present, laser measurement methods for gaseous pollutants are experimental and are unlikely to become fully operational within the next year or two; therefore, the discussion here will not further explore the various approaches.

An acoustic radar (or sodar) can be used to measure meteorological conditions aloft, and has been used to characterize the air pollution meteorology of the San Francisco Bay Area (Russell and Uthe, 1978), in Los Angeles (Edinger, 1975), and in other cities. Commercially available instruments will display the locations and extent of temperature inversions and thus define the extent of the mixing layer. Their vertical range is typically 1 km, although longer range instruments have been built. Lidar will also provide the same type of information; Russell, et al (1974), contrast the capabilities of these two techniques.

Doppler acoustic radar can provide continous data on winds aloft. Recent developments have allowed the measurement of winds up to 1 km above ground level. Such Doppler instruments, when combined with airborne measurements of pollution, offer a workable short-term approach to complete pollutant transport monitoring. Instruments have recently become commercially available from several firms in the United States and Europe. A paper by Peters, et al (1978), critically analyzes the capabilities of some acoustic Doppler approaches. Remote wind measurements can also be made by Doppler lidar (Post, et al, 1978) and by microwave radar (Chadwick, et al, 1976), but at significantly higher cost.

Remote measurement sensors vary widely in cost. At the upper end, laser systems can cost in excess of $200,000. Doppler acoustic radar lies in the $25,000 to $50,000 range. The correlation spectrometer costs less, and the simple acoustic radar is the lowest priced at about $10,000. Operating costs also vary widely depending upon the need for an operator and the degree of automation of the data recording method of any given approach. At this time, only the correlation spectrometer and acoustic sounders (including Doppler units) are commercially available.

2.2 COMPARATIVE EVALUATION

The methods discussed in the preceding section have offered a spectrum of capabilities and costs. We have established a number of criteria for evaluating their usefulness in obtaining oxidant and precursor measurements to be used in developing oxidant control strategies. In formulating these criteria, we assumed that these methods would be applied by state and local air pollution agencies during the oxidant seasons, in the next two to five years.

The evaluation criteria are:

- Initial cost – should be as low as possible.
- Operating cost – should be as low as possible.
- Manpower requirements – should be relatively low.
- Required technical expertise to operate – should be within capability of most state and local air pollution control agencies.
- Portability – ability to use in more than one area during the same oxidant season would be desirable.
- Measurements made – O_3 mandatory, NO/NO_2 very desirable, HC desirable, winds mandatory (if at all possible).
- Location of measurements – both surface and aloft is most desirable.
- Site specificity – approach should be usable equally well in several locations.

An evaluation of each method against these criteria is shown in Table 1. The overall costs and benefits of the various methods have been subjectively ranked, with the evaluation based on the situation which is expected to prevail in most urban areas where oxidant and precursor transport is of interest. The ranking could be substantially different for a specific case where a particular capability, for example, portability, was important. A cost-benefit index, based on this subjective ranking, is also shown.

Based on this subjective analysis, fixed stations (Method A) appear to be both the most efficient and the most cost-effective oxidant transport measurement method. Aircraft measurements, using a portable instrument package (Method E) are less effective in terms of benefits alone, but may be as cost-effective as the fixed sites. Free balloon and tethered balloon soundings (Methods G and H) are tied for third place in the cost-benefit ranking, mainly because of their extremely low cost. Towers and dedicated aircraft (Methods C and D) are tied for fourth place overall, with the high cost of the aircraft being the major factor in placing it this far down the list.

Remote sensing could not be ranked as a group because of the wide variety of capabilities and costs. The absence of an O_3 measurement capability is a serious drawback, however. Acoustic sensing of winds and atmosphere stability may be a very effective tool in conjunction with other techniques for pollution sensing.

To provide further evaluation of these approaches, methods A, D, E, G, and H were tested in Philadelphia in the summer of 1978. A description of the tests performed and a more detailed evaluation of these five techniques are provided in the following chapters.

Table 1. EVALUATION OF OZONE AND PRECURSOR MEASUREMENT METHODS, AS APPLIED TO THE TYPICAL URBAN OXIDANT TRANSPORT SITUATION.

Method	Costs				Benefits				Subjective Ranking (c)		
	Initial Cost (a)	Approximate Operating Cost (b)	Manpower Needs	Technical Expertise Required	Portable?	Measures	Location of Measurements	Site Specific	Cost	Benefit	Cost-Benefit Index (e)
A. Surface measurements, fixed sites	Moderate	Moderate	Low	Moderate	No	O_3, NO/NO_2, HC, wind	Surface, fixed	No	4	1	5
B. Surface measurements, moving vehicle	High	Moderate to high	High	Moderate	Yes	O_3, NO/NO_2, wind	Surface, moving	No	6	4	10
C. Tower measurements	Moderate to high	Moderate	Moderate	Moderate	No	O_3, NO/NO_2, HC, wind	Aloft, fixed	Yes requires existing tower	5	5	10
D. Airborne measurements, dedicated aircraft	High	Moderate	High	High	Yes	O_3, NO/NO_2, HC	Aloft, moving	No	8	2	10
E. Airborne measurements, portable instrument package	Low	Low	High	Low	Yes	O_3, NO/NO_2	Aloft, moving	No	3	3	6
F. Airborne measurements, manned balloon	High	Moderate	High	High	Yes	O_3, NO/NO_2, HC, wind	Aloft moving	No	7	9	16
G. Soundings, free lift balloon	Low	Low to moderate	High	Low	Yes	O_3, wind	Aloft, semi-fixed	No	1	7	8
H. Soundings, tethered balloon	Low	Low to moderate	High	Low	Yes	O_3, wind	Aloft, fixed	No	2	6	8
I. Remote sensing	(d)	(d)	Moderate to low (g)	(d)	(d)	NO_2, wind	Aloft, by sensor on surface	(f)	(d)	8(f)	(g)

(a) Low: <\$25K
Moderate: \$25 - \$100K
High: >\$100K

(b) Low: <\$25K for one city
Moderate: \$25 - \$100K for one city
High: >\$100K for one city

(c) From 1 through 9, with 1 the highest ranked (greatest benefit or lowest cost)

(d) Depends on specific method - ranges from low for monostatic acoustic radar to moderate for correlation spectrometer and Doppler acoustic radar to high for laser systems

(e) Sum of cost ranking and benefit ranking; low value is best

(f) See text for discussion

(g) Depends on specific method used

3. FIELD PROGRAM TO EVALUATE SELECTED MEASUREMENT TECHNIQUES

Five selected methods for measuring the transport of photochemical pollutants into Philadelphia were tested in the summer of 1978. These methods were: (1) a continuous surface monitoring network; (2) a dedicated instrumented helicopter; (3) a light aircraft equipped with a portable ozone/temperature instrument package; (4) a free lift balloon ozonesonde; and (5) a tethered balloon ozonesonde. In addition, grab and time-integrated hydrocarbon samples were collected at four of the surface monitoring stations and by the helicopter and light aircraft on selected days for species analysis. The surface monitoring stations were operational during July, August, and September of 1978, while measurements using aircraft and balloons were made on 15 days during August and September.

3.1 OBJECTIVES OF THE FIELD PROGRAM

The primary objective of the field program was to demonstrate and evaluate the five selected methods for measuring the transport of photochemical pollutants into Philadelphia. Other objectives included:

1. Assessment of typical levels of O_3, NO, NO_2, and non-methane hydrocarbons transported into Philadelphia at the surface and in layers aloft.

2. Evaluation of species composition of hydrocarbons transported into Philadelphia.

3.2 PROGRAM DESIGN

To achieve the objectives of the field program, AV established five surface monitoring stations around Philadelphia. Continuous measurements of ozone, nitrogen oxides, non-methane hydrocarbons, wind speed and direction, temperature, and solar radiation were made at each of these stations during July, August, and September of

1978. An acoustic radar to collect mixing height information was also installed at one of the stations.

Aircraft measurements of O_3, NO, NO_x, visible light scattering, temperature, and dew point were performed by the EPA-Las Vegas Environmental Monitoring and Support Laboratory (EMSL) on 12 days in August.

The portable ozone/temperature package, the free balloon ozonesonde system, and the tethered balloon ozonesonde system were tested in August and September. In addition, grab and time-integrated air samples were taken on the ground and in the air on seven days during August and September. Those samples were analyzed by Scott Environmental Technology, Inc. for hydrocarbon species (C_2 through C_{10} and aromatics).

More detailed descriptions of each segment of the field program are presented below.

3.3 SURFACE MEASUREMENTS AT FIXED SITES

The surface monitoring program consisted of five stations set up specifically for the study and six supplemental stations whose data were also used in the analysis. The locations of all stations are shown in Figure 2.

The parameters monitored continuously at Sites 1 through 5 included: O_3, NO/NO_x, THC/CH_4, wind speed, wind direction, temperature, and solar radiation. Mixing height was also measured at Site 1. All of the equipment used, except the acoustic radar, was supplied by the EPA. The specific instruments used at these stations are listed in Table 2. The methodologies used for the measurement of oxides of nitrogen and ozone are EPA reference methods. There are currently no EPA guidelines on the measurement of non-methane hydrocarbons.

Ozone data collected at all supplemental sites and NO/NO_x data collected at Franklin Institute and South Broad Sites were also included in the data analysis.

The purpose of each of the stations is discussed below.

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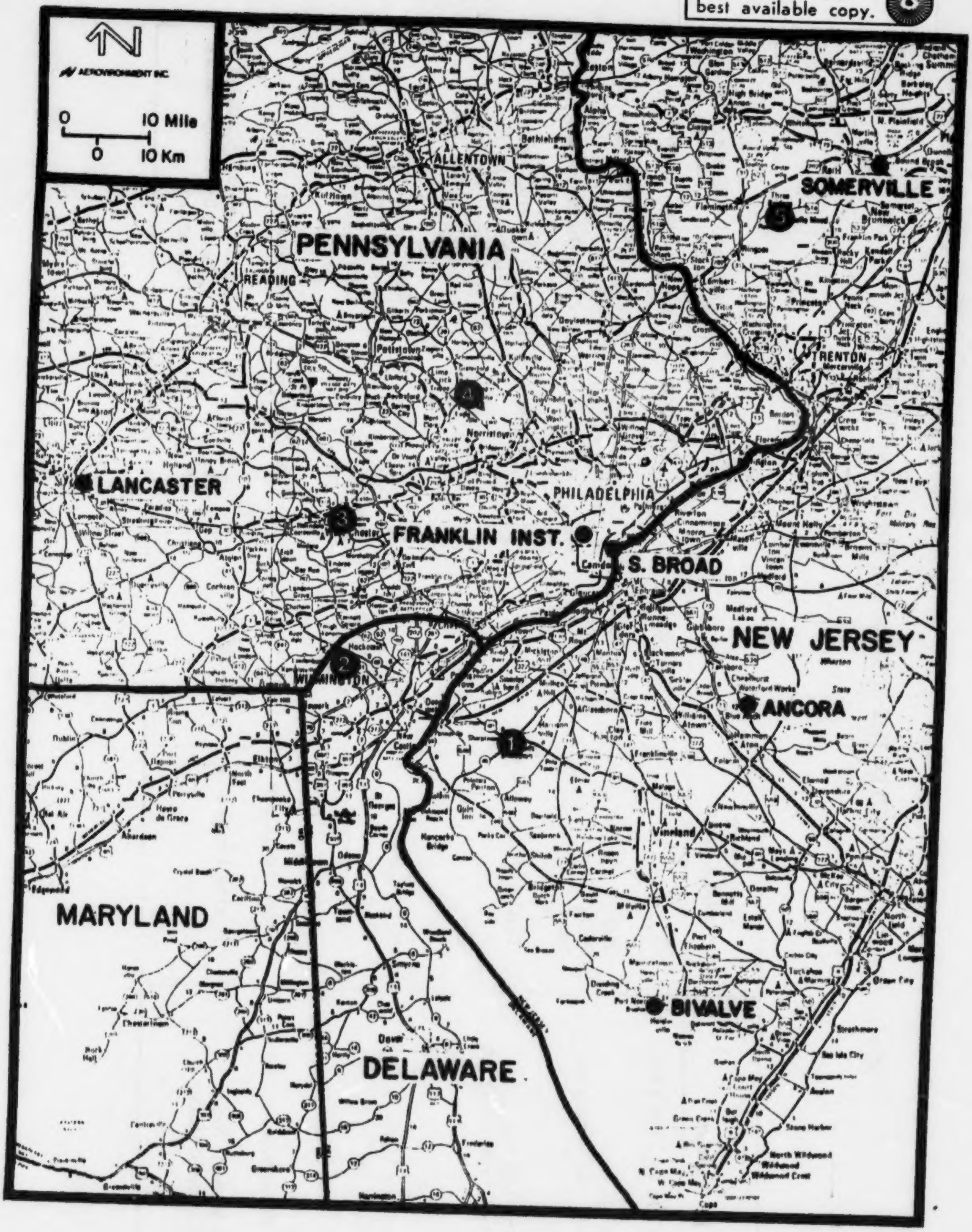

N
AEROVIRONMENT INC.
0 10 Mile
0 10 Km
ALLENTOWN
SOMERVILLE
5
PENNSYLVANIA
READING
TRENTON
4
LANCASTER
PHILADELPHIA
3
FRANKLIN INST.
S. BROAD
NEW JERSEY
2
WILMINGTON
ANCORA
1
MARYLAND
BIVALVE
DELAWARE

FIGURE 2. Locations of monitoring sites. Numbered sites are transport stations and dots represent supplemental stations.

Table 2. EQUIPMENT USED IN THE SURFACE MONITORING NETWORK.

Instrument	Parameter Measured	Range	Accuracy	Method of Detection
Bendix 8002 O_3 Analyzer	O_3	0-0.5 ppm	±0.005 ppm	Chemiluminescent
Bendix 8101 $NO/NO_2/NO_x$ Analyzer	NO NO_2 NO_x	0-0.5 ppm 0-0.5 ppm 0-0.5 ppm	±0.015 ppm ±0.015 ppm ±0.015 ppm	Chemiluminescent Chemiluminescent Chemiluminescent
Beckman 6800 Air Quality Chromatograph	THC	0-10 ppm	±0.1 ppm	Gas Chromatography - Flame Ionization
	CH_4	0-10 ppm	±0.1 ppm	Gas Chromatography - Flame Ionization
Climatronics Mark I Wind System	Wind Speed Wind Direction Temperature	0-22 m/s 0-540° -7 to 49°C	±.2 m/s ±5° ±1°C	Wind Cups Wind Vane Thermistor in a radiation shield
Eppley Pyranometer	Solar Radiation	0-1.5 Ly/min	±0.02 Ly/min	Pyranometry
AeroVironment Inc. 300 Acoustic Radar	Mixing Height	30-1000 m	±10 m	Scattering of Acoustic Waves by Temperature Structure

3.3.1 Sites 1, 2, and 3

These stations were located upwind of Philadelphia under the prevailing flow, which was determined to be from the south-southwest to west direction. Site 1 was located near Woodstown, New Jersey, approximately 40 km south-southwest of the Philadelphia urban core. Site 2 was located near Hockessin, Delaware, approximately 50 km southwest of the Philadelphia urban core. Site 3 was located near Downingtown, Pennsylvania, approximately 50 km west of the Philadelphia urban core. Figure 3 shows the monitoring station at Site 1. The monitoring stations at Sites 2, 3, 4, and 5 were identical to the one at Site 1.

The purpose of these sites was to monitor the ozone and precursors transported into the city, both along the surface and aloft. Surface stations can provide an indication of transport aloft, since ozone and precursors trapped aloft overnight are brought to the ground through turbulent vertical mixing after the breakup of the nocturnal radiative inversion. In areas upwind of the city, where emissions of ozone precursors are generally insignificant, ozone readings between about 1100 and 1300 local daylight time (LDT), after the vertical mixing has occurred, have been suggested by U.S. EPA (1977) to be most indicative of ozone levels transported aloft.

3.3.2 Site 4

This site was located 35 km northwest of Philadelphia near Collegeville, Pennsylvania. The purpose of this site was to determine the effect of ozone and precursors transported from upwind areas on the ozone and precursors which would be measured at the urban core, in the absence of the urban emissions. Measurements taken at Sites 1, 2, and 3 quantify the ozone and precursors moving into the urban area. However, on the way to the urban core, these pollutants diffuse and undergo photochemical reactions. Measurements taken at Site 4 thus define what the ozone and precursor levels would be at the urban core if there were no significant emissions in the path between the upwind sites and the urban core. The difference between pollutant levels at Site 4 and the urban core can then be considered to be a consequence of the urban emissions. When flow was from the west or northwest, this site acted as an upwind site.

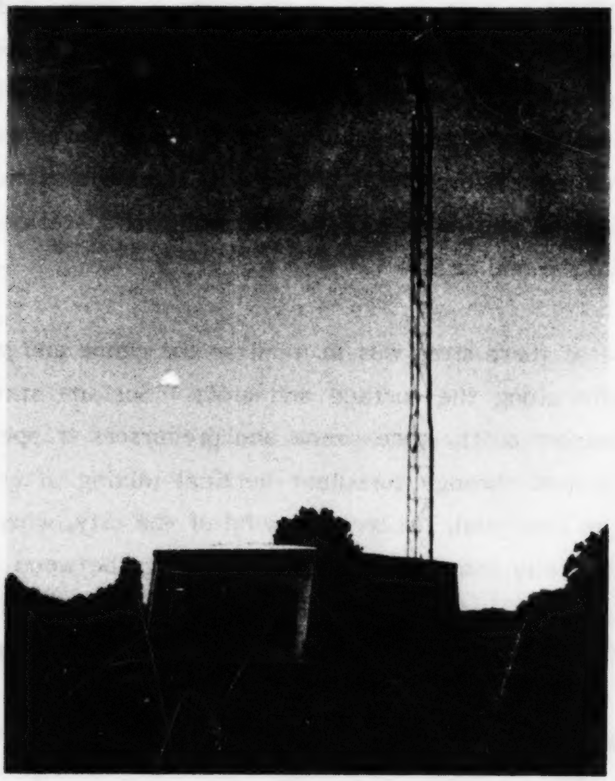


FIGURE 3. Monitoring station at Site 1.

3.3.3 Site 5

This site was located 65 km north-northeast of Philadelphia near Ringoes, New Jersey. It was downwind of Philadelphia when the prevailing flow was from the southwest sector and served to monitor the peak ozone concentration resulting from ozone and precursors transported into Philadelphia and precursors emitted in the Philadelphia urban core.

3.3.4 Lancaster and Bivalve

Lancaster was located about 95 km west of Philadelphia, and Bivalve was located about 90 km south of Philadelphia. The purpose of these sites was similar to that of Sites 1, 2, and 3. Ozone data from Lancaster and Bivalve were used to quantify ozone concentrations upwind of Philadelphia.

3.3.5 Ancora

This site was located about 45 km southeast of Philadelphia. Its purpose was similar to that of Site 4. Under the prevailing flow, ozone data at this site would indicate what the ozone concentration at the urban core would be in the absence of urban emissions. It would act as an upwind site when the flow was from the south or southeast and a downwind site when the flow was from the north or northwest.

3.3.6 Franklin Institute and South Broad Street

These sites were both located in downtown Philadelphia and collected oxides of nitrogen and ozone data. These data were used in the study to provide information on the concentrations of ozone and oxides of nitrogen in the urban core.

3.3.7 Somerville

This station served the same purpose as that of Site 5. It is located about 80 km northeast of Philadelphia.

3.4 AIRBORNE MEASUREMENTS BY DEDICATED INSTRUMENTED AIRCRAFT

The primary objective of the aircraft measurements was to obtain vertical profiles and cross sections of ozone and precursors in order to determine interrelationships of these pollutant concentrations at the surface and aloft. From these profiles and cross sections, typical levels of ozone and precursors transported into the study city in layers aloft over various time periods during days of high photochemical activity could also be determined.

Aircraft measurements were performed by the EPA - Las Vegas Environmental Monitoring and Support Laboratory between August 8 and 25, 1978. The aircraft used was a Bell UH/1H helicopter (Figure 4). Parameters measured included O_3, NO, NO_x, visible light scattering, temperature, and dew point versus altitude, location, and time. The methodologies for measuring ozone and oxides of nitrogen are EPA reference methods. In addition, hydrocarbon grab samples were taken for species analysis. The hydrocarbon sampling will be discussed in more detail later in this chapter. Table 3 lists the instruments used.

The aircraft (helicopter) measurement program consisted of 12 days of intensive vertical soundings and horizontal traverses over and upwind of the study city. The choice of these 12 days was based on forecasts predicting significant photochemical activity along with consistent transport from upwind areas.

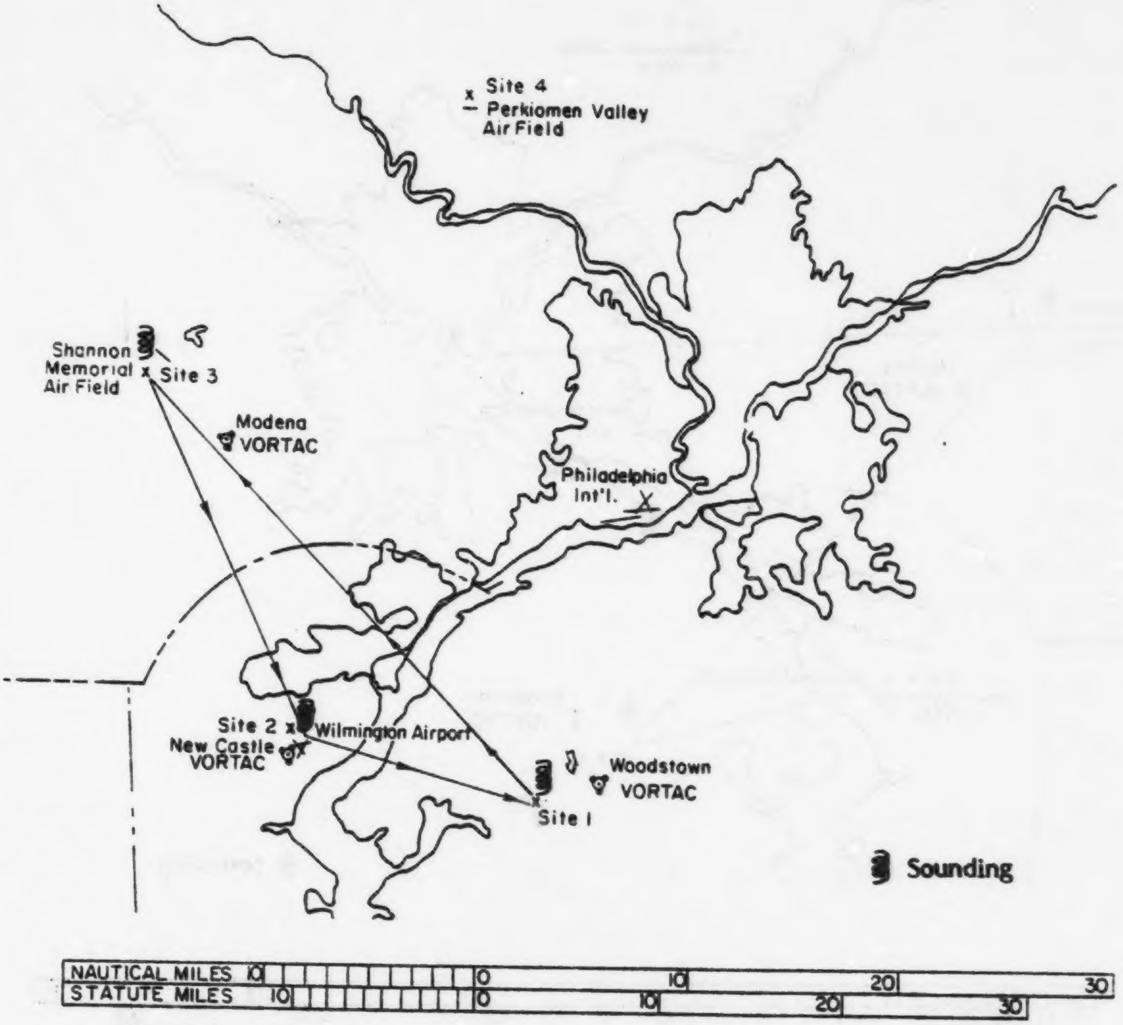
On each measurement day, two flights were made: one in the early morning hours (generally between 0400 - 0630 EDT) and one in the late morning (generally between 0900 - 1130 EDT). Each flight consisted of vertical soundings over three surface monitoring stations from as close to the ground surface as possible up to 2 km above ground level (AGL), and a horizontal traverse between the stations at the elevation where maximum ozone levels were observed. Figures 5 and 6 show the typical flight patterns during the early and late morning flights. Exact flight paths taken on each sampling day have been documented elsewhere (Hancock, 1978).

The early morning flight was designed to provide information concerning vertical profiles and horizontal gradients aloft of ozone and precursors upwind. Thus, traverses

FIGURE 4. Dedicated EPA-Las Vegas instrumented UH-1H helicopter.

Table 3. PARAMETERS MEASURED BY HELICOPTER AND INSTRUMENTS USED.

Parameter	Instrument
Hydrocarbons	One liter grab samples using evacuated stainless steel canisters
Ozone	REM 612 B chemiluminescent analyzer
$NO/NO_2/NO_x$	Monitor Labs 8440 chemiluminescent analyzer
Light Scattering	MRI 1550 nephelometer
Temperature/Dew Point	EG&G 137 CL-S1ATH
Static pressure (altitude)	National Semiconductor LX3702A
Position	(2) Collins DME 40 and (1) VOR-31A



Site 4
Perkiomen Valley Air Field
Shannon Memorial Air Field
Site 3
Modena VORTAC
Philadelphia Int'l.
Site 2
Wilmington Airport
New Castle VORTAC
Woodstown VORTAC
Site 1
Sounding
NAUTICAL MILES 10 0 10 20 30
STATUTE MILES 10 0 10 20 30

FIGURE 5. Typical flight pattern followed during 0400 EDT flight.

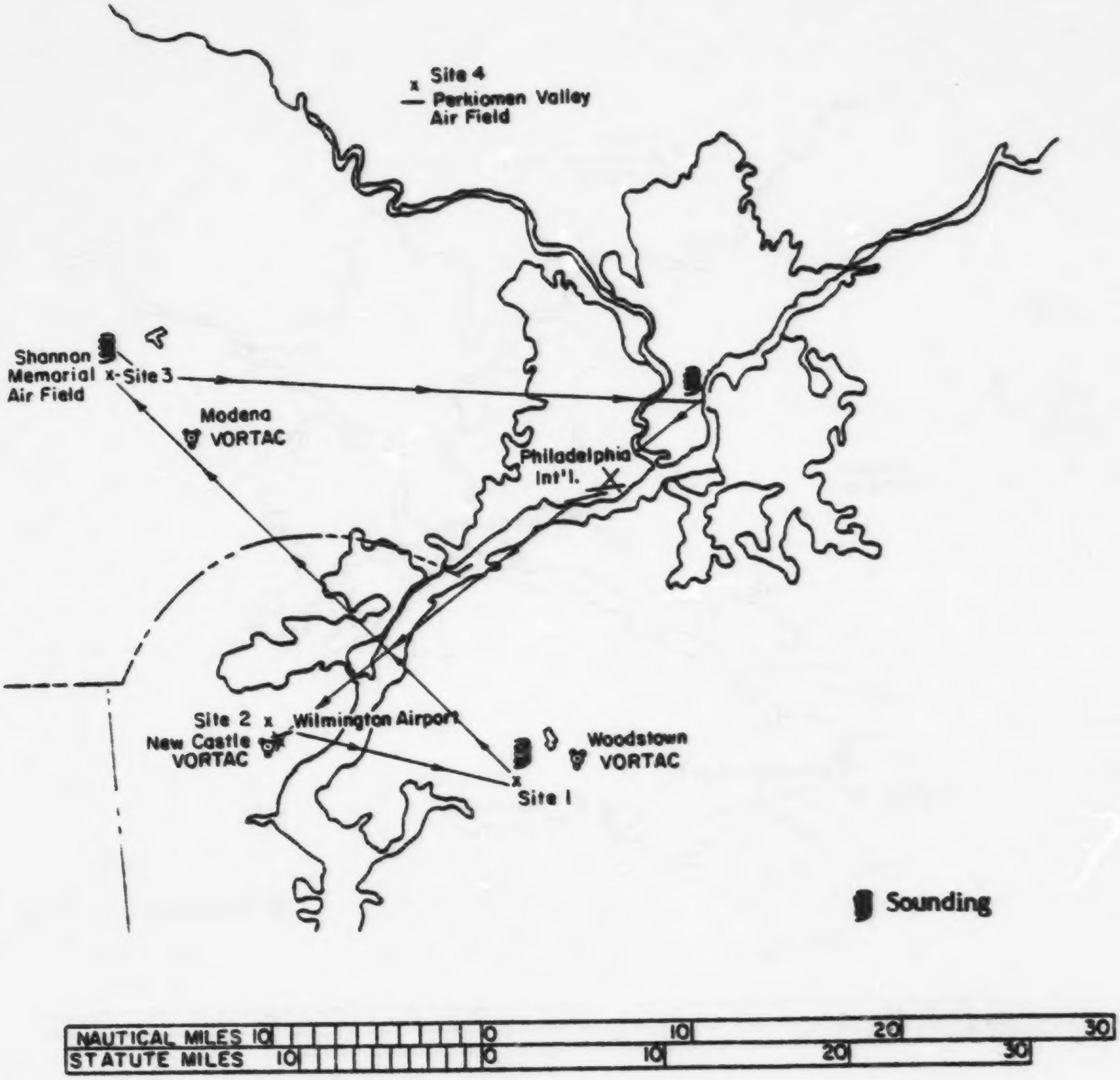

Site 4
Perkiomen Valley Air Field
Shannon Memorial Air Field
Site 3
Modena VORTAC
Philadelphia Int'l.
Site 2
Wilmington Airport
New Castle VORTAC
Woodstown VORTAC
Site 1
Sounding
NAUTICAL MILES 10 0 10 20 30
STATUTE MILES 10 0 10 20 30

FIGURE 6. Typical late morning flight pattern.

were made only along the upwind edge of the study area and soundings were taken only over the three upwind sites. The later morning flight was designed to provide information concerning vertical profiles and horizontal gradients aloft of ozone and precursors upwind, as well as the vertical distribution of ozone and precursors over the downtown area. Thus, soundings were made over two upwind sites and also over downtown Philadelphia.

A special pattern designed for study of a stagnant air mass was flown on August 15, 1978. On that day, two flights were made, each one consisting of a spiral sounding near Site 2, a traverse to the downtown area, where a spiral sounding was made, and a traverse back to Site 2, where a final sounding was made.

3.5 AIRBORNE MEASUREMENTS BY A PORTABLE INSTRUMENT PACKAGE

The second airborne measurement approach tested was the portable instrument package as described in Chapter 2. The package consisted of a flyable, battery operated ozone/temperature analyzer which could be placed in a light airplane with no aircraft recertification requirement. For this project, a Cessna 172 was used (see Figure 7). The instrument was a Columbia Instruments Model 2000 chemiluminescent O_3 analyzer. The operating gas was a non-flammable ethylene mixture (Ethychem) in a low pressure container, which was exempt from the hazardous materials transportation regulations. The analyzer has a range of 0 to 0.5 ppm and an accuracy of ± 0.005 ppm when operated with pure ethylene; the performance is degraded slightly when Ethychem is used. This analyzer meets EPA reference method designation specifications when ethylene is used but does not meet these specifications when Ethychem is used.

It was originally planned that a Columbia Scientific Model 2200 chemiluminescent NO/NO_x analyzer, which was under development at that time, would also be a component part of the portable instrument package. Unfortunately, the instrument was not ready by the time evaluations of various measurement techniques were under way.

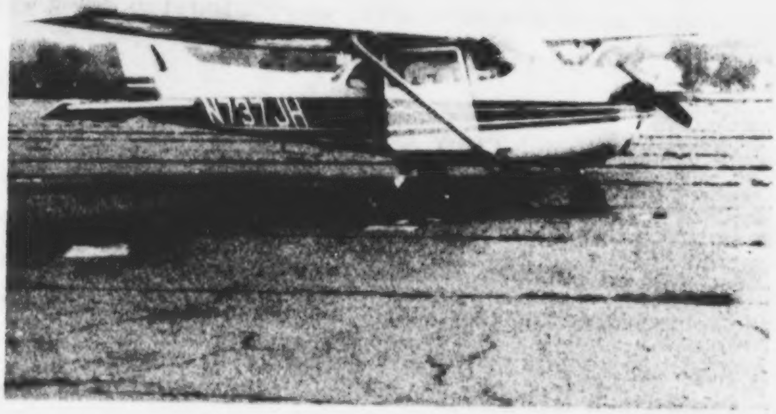


FIGURE 7. Cessna 172 aircraft used for flying the portable instrument package.

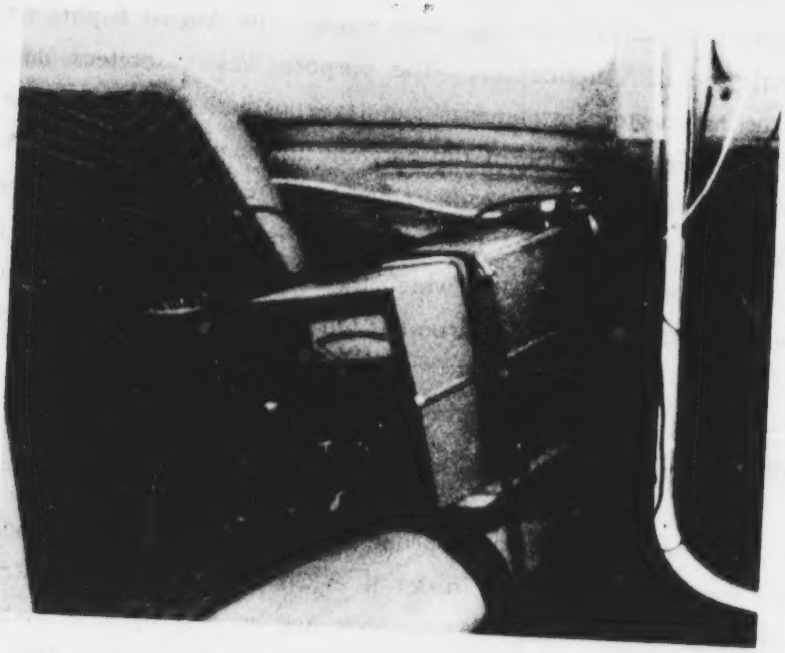


FIGURE 8. Portable instrument package and recorder strapped to passenger's seat of aircraft.

Samples to the ozone analyzer were provided by 6 mm diameter Teflon line threaded through the cabin fresh air inlet of the aircraft. The temperature sensor was also installed in the same fresh air vent as the sample tube. The readings from the analyzer and the temperature sensor were recorded on a battery-operated Linear Instruments chart recorder. The analyzer and the chart recorder were strapped to the passenger seat of the aircraft as shown in Figure 8.

The portable instrument package was flown on five days in August and three days in September. Table 4 presents a summary of dates and times of sounding with the package and sites over which soundings were made. The August flights were made in conjunction with the EPA helicopter. The purpose was to collect data with the package and the helicopter instruments simultaneously at the same locations, thus allowing a performance evaluation of the portable instrument package. The free lift balloon ozone sounding system (to be described later) was not ready for testing until September, by which time the EPA helicopter was no longer available. In order to obtain some ozone profile data against which the free lift balloon ozone sounding data could be compared, the portable instrument package was flown on three days in September.

3.6 SOUNDINGS BY OZONESONDE BENEATH A FREE LIFT BALLOON

A third airborne measurement approach tested was a free lift balloon ozone sounding. This method is described in detail in Chapter 2. As demonstrated in this study, it consisted of a Mast 730-9 ozonesonde and an Atmospheric Instrumentation Research Company AS-1C three-channel airsonde (see Figure 9). The radio transmitter on the airsonde transmits temperature, pressure and ozone data to an Atmospheric Instruments Research Company TS-2A Ground Station (see Figure 10).

The ozonesonde, in its original form, measures total oxidants and thus responds also to SO_2 and NO_2 in the ambient air. During the tests an absorber column packed with glass fiberpaper impregnated with CrO_3 and H_2SO_4 (Mast Model 725-30 SO_2 filter kit) was added to the intake of the ozonesonde. The column removes SO_2; tests indicate that the removal of SO_2 is 100% complete if the column is used for no longer than 540 ppm-hr of sampling. The absorber also completely

Table 4. DATES AND TIMES OF FLIGHTS USING THE PORTABLE INSTRUMENT PACKAGE, AND SITES OVER WHICH VERTICAL PROFILE MEASUREMENTS WERE TAKEN.

Date	Time in EDT (beginning of flight)	Sites
8/18	0902	1,3
8/19	1325	1
8/22	0948	1,3
8/23	1000	2,4
8/24	1618	1
9/21	0700	1
9/21	0940	1
9/27	0740	1,2,3
9/27	1500	1
9/27	1800	1
9/30	0700	1
9/30	1100	1
9/30	1500	1
9/30	1800	1

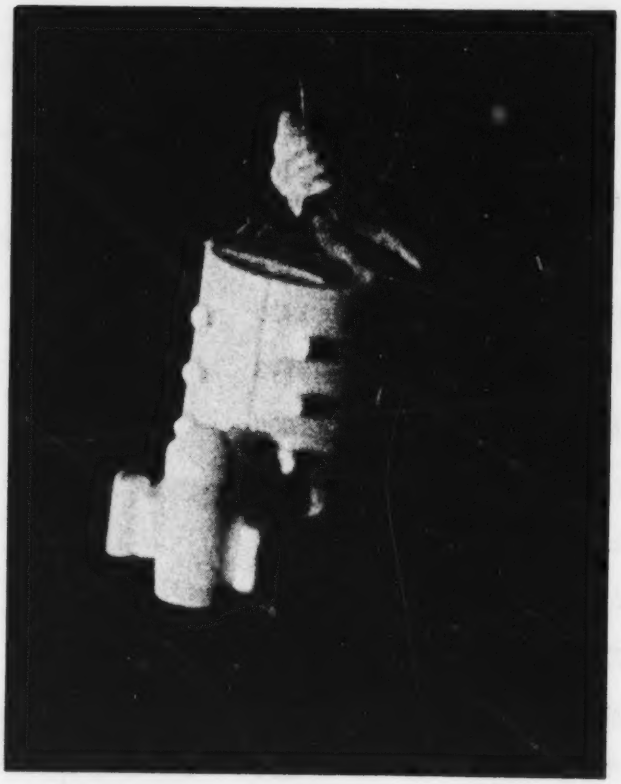


FIGURE 9. Mast 730-9 ozonesonde.

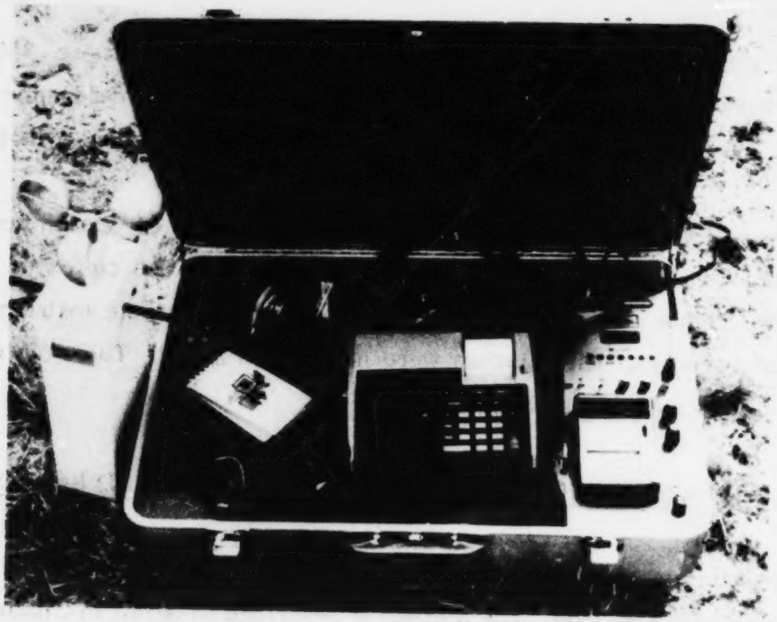


FIGURE 10. Atmospheric Instruments Research Company ozonesonde ground station.

converts NO to NO_2, which gives about 10% positive interference to the O_3 measurements. The worst case during the ozone sounding days had an NO_x concentration of 0.075 ppm which could result in approximately 0.008 ppm of O_3 overestimation. Considering that the ozonesonde has an accuracy of $\pm$ .01 ppm, its use without also removing the NO_2 beforehand seems justified. The range of the ozonesonde is from 0 to 0.50 ppm. Presently, the ozonesonde does not meet EPA equivalency requirements.

The package was flown under a helium-filled, free-rise 350 gram balloon. Tracking with a single theodolite was performed in order to determine wind speed and direction. (The pressure channel allows calculation of the package altitude.)

Eleven flights were made on three different days in September. Four of the ozonesondes were found to have linearity problems and data collected were discarded. Six of these flights were made in conjunction with the portable instrument package for comparison purposes. All launches were made from Site 1. Table 5 presents dates and times of all successful launches.

3.7 SOUNDINGS BY OZONESONDE BENEATH A TETHERED BALLOON

A fourth airborne measurement approach tested was that of an ozonesonde beneath a tethered balloon. The method is described in detail in Chapter 2. As used in this study, it consisted of a Mast 730-9 ozonesonde and an Atmospheric Instrumentation Research Company TS-2A tethersonde supported by a 4.25 m^3 kytoon (Model TS-1BR-2) with a TS-2A Ground Station. Figure 11 shows the tethered balloon ozonesonde system. An absorber column packed with glass fiber paper impregnated with CrO_3 and H_2SO_4 was also added to the intake of the ozonesonde for removing SO_2. The range and accuracy of this system in measuring ozone are identical to those of the ozonesonde used with free lift balloons. The combination of the ozonesonde and the tethersonde made it possible to measure ozone, temperature, relative humidity, pressure, wind speed, and wind direction, all as functions of elevation.

Table 5. DATES AND TIMES OF SUCCESSFUL LAUNCHES OF OZONESONDE BENEATH A FREE LIFT BALLOON.

Date	Time (EDT)
9/24	0807 1055
9/27	1207 1516 1905
9/30	0720 1630

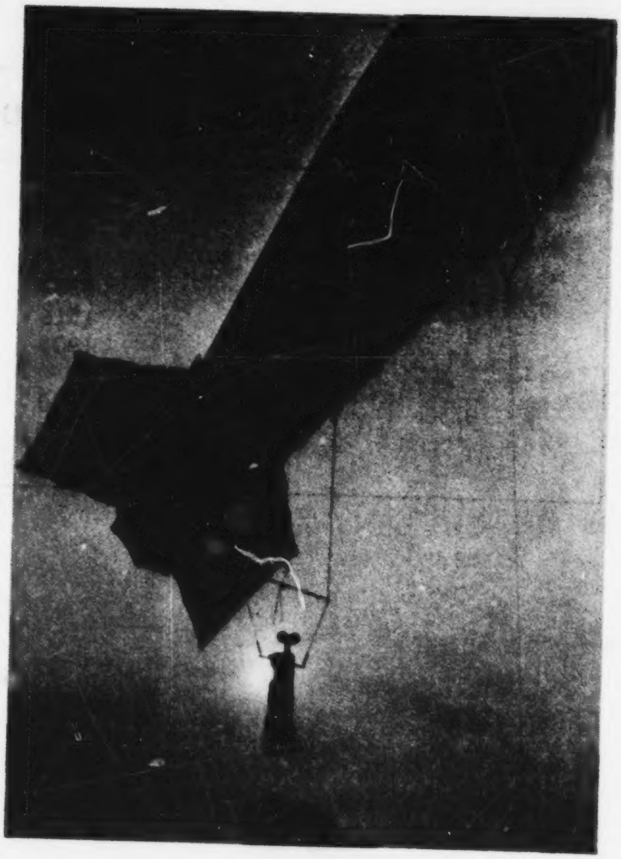


FIGURE 11. Tethered balloon ozonesonde system.

The system was flown on four days for a total of eleven flights. Table 6 summarizes the dates and times of tethersonde flights. All flights were made at Site 1.

3.8 HYDROCARBON SAMPLING FOR SPECIES ANALYSIS

The purpose of this phase of the program was to provide information on the hydrocarbon species as they are transported into the urban area.

There were two parts to the sampling program: (1) Integrated samples at the ground level were collected at each of Sites 1, 2, 3, and 4; and (2) grab samples were collected aloft using the EPA helicopter over Sites 1, 2, 3, and downtown Philadelphia, and, on one occasion, over Site 4.

Evacuated one-litre stainless steel containers were used to collect the ambient air samples for analysis. Prior to sampling, the containers were cleaned by repeated evacuation and purging with hydrocarbon-free nitrogen followed by heating and re-evacuation.

Ground-level sampling at the monitoring sites was performed by using the containers in series with a solenoid valve connected to the site's sampling manifold. At a preset time, the solenoid valve was actuated by a timing device for one hour during which ambient air "leaked" into the partially opened sampling container. Thus, some time integration was achieved. The rate at which the container was filled was not constant. At the beginning of the hour, the flow rate was about 50 cc/min. The rate dropped to zero at the end of the sampling period.

Aircraft samples were instantaneous grab samples taken through the sampling manifold. The sampling procedure followed, with minor deviations, was the same from day to day.

During the early morning helicopter flight (0400 - 0630 EDT), ground samples were taken at Sites 1, 2, 3, and 4. Three aircraft samples were taken over each of Sites 1, 2, and 3. One of these samples was taken as close to the ground as possible

Table 6. DATES AND TIMES OF LAUNCHES OF OZONESONDE BENEATH A TETHERED BALLOON.

Date	Time (EDT)
8/24	1112
	1650
9/21	0759
	1020
	1117
	1328
9/27	0922
	1313
	1613
9/30	0845
	1341

and the other two above the surface based inversion (at approximately 1 and 1.5 km MSL).

During the late morning flight (0900 - 1130 EDT), ground samples were taken at Sites 1, 3, and 4 and one aircraft sample was taken over each of Sites 1, 3, and downtown Philadelphia at an elevation of about 1 km. Thus, both horizontal and vertical hydrocarbon profiles were defined over upwind areas during both flights. In addition, information about hydrocarbon species aloft over downtown and at the surface at Site 4 was also obtained.

Samples were analyzed by Scott Environmental Technology for hydrocarbon species C_1 - C_{10} using a Perkin-Elmer 900 Gas Chromatograph.

Samples were taken on seven photochemically active days*. A total of 126 samples were taken. Table 7 summarizes the sample collection times.

3.9 QUALITY ASSURANCE

This section summarizes the procedures used to assure data quality for the field program. Specifically, the calibration methods and frequency, station check methods and frequency, and audit and interlaboratory tests are described for the surface monitoring program and the airborne measurement program.

3.9.1 Surface Monitoring Program

The equipment listed in Table 2, except for the acoustic radar, was tested and furnished to AeroVironment by the EPA prior to field use. The equipment and recording devices were installed in environmentally-controlled shelters to meet the manufacturers' specifications at each of the five monitoring stations.

In the beginning of the program, however, temperatures at Sites 2, 3, 4, and 5 often exceeded the upper limit of the recommended operating temperature range of

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*The criteria for a photochemically active day are given on pp. 63-64.

Table 7. FREQUENCY, TIMES, AND LOCATIONS OF HYDROCARBON SAMPLES COLLECTED FOR SPECIES ANALYSES.

Date	Altitude	No. of Samples Taken at Approx. 0500 EDT				No. of Samples Taken at Approx. 1100 EDT				
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4	Down town Phila-delphia
8/8	Surface	1	1			1			1	
	Aloft	3	3	3		1		1		1
8/9	Surface	2	1	2	1	1		1	1	
	Aloft	3	3	3		2		2		1
8/16	Surface	1	1	1	1	1		1	1	
	Aloft	3	2	3		1		1		1
8/18	Surface	1	1	1	1	2		1	1	
	Aloft	3	2	3		1		1		1
8/23	Surface	1	1	1	1	1		1	1	
	Aloft	3	2				1			1
8/24	Surface	2	1	1	2	1	1		1	
	Aloft	3	3		3	1			1	1
9/27	Surface	2	1	1		1	1	1		
	Aloft	3	1	3						
TOTAL		31	24	22	9	14	3	10	7	6

Total Samples Collected: 126

Table 7. FREQUENCY, TIMES, AND LOCATIONS OF HYDROCARBON SAMPLES COLLECTED FOR SPECIES ANALYSES.

Date	Altitude	No. of Samples Taken at Approx. 0500 EDT				No. of Samples Taken at Approx. 1100 EDT				
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4	Down town Phila-delphia
8/8	Surface	1	1			1			1	
	Aloft	3	3	3		1		1		1
8/9	Surface	2	1	2	1	1		1	1	
	Aloft	3	3	3		2		2		1
8/16	Surface	1	1	1	1	1		1	1	
	Aloft	3	2	3		1		1		1
8/18	Surface	1	1	1	1	2		1	1	
	Aloft	3	2	3		1		1		1
8/23	Surface	1	1	1	1	1		1	1	
	Aloft	3	2				1			1
8/24	Surface	2	1	1	2	1	1		1	
	Aloft	3	3		3	1			1	1
9/27	Surface	2	1	1		1	1	1		
	Aloft	3	1	3						
TOTAL		31	24	22	9	14	3	10	7	6

Total Samples Collected: 126

86°F. This was because of a combination of air conditioner malfunctions and the insufficient capacity of the air conditioners. Those problems were corrected and by August 1, all stations were operating within the specified temperature range.

3.9.1.1 Calibration of Air Quality Instruments

Multipoint calibration of all air quality instruments at each station was performed by AV personnel bi-weekly throughout the measurement program. In addition, calibration of an instrument was carried out whenever any of the following conditions occurred: (a) the control limit for the span check as specified in the Station Check List Log was exceeded; (b) after repair of a malfunctioning analyzer; (c) after replacement of major components of an analyzer; and (d) when the audit results exceeded the limits established (see Audit Section). Zero plus a minimum of four calibration points equally spaced over the analyzer range were used to generate a calibration curve. A "master" calibrator was used for all of the multipoint calibrations to ensure data comparability. The purpose of the multipoint calibrations was twofold: (a) to check the instrument linearity; and (b) to assign the values of the on-site calibration sources so that they would also be NBS traceable.

Dynamic calibration of the air quality instruments was carried out for NO-NO_2-NO_x and O_3 analyzers by use of a Bendix calibrator. For NO and NO_x channels, an NBS SRM cylinder gas containing approximately 50 ppm NO in N_2 was diluted to ambient levels for the calibration. For the NO_2 channel, the technique of gas phase titration (GPT) of NO and O_3 prescribed by EPA (Federal Regulation, Title 40, Part 50, Appendix F) was employed.

For the O_3 analyzers, the calibrator's O_3 output was determined on-site by both the GPT technique and UV photometry method (Federal Register, Vol. 44, No. 28, PR 8221-8233, February 8, 1978). For the former, the data obtained during the NO_2 calibration was conveniently utilized, and for the latter, a modified Dasibi Model 1003 AH ozone monitor served as a transfer standard. Although the GPT results were used as the O_3 reference method for this project, the UV photometry calibration results were also documented.

For the THC/CH_4 instruments, two compressed gas cylinders containing approximately 0 and 8 ppm of CH_4 in an ultrapure air were used for the calibration. Multipoint calibration was accomplished by using an AV Model BB-100 dilution system. The CH_4 cylinder gas used was NBS traceable.

The NO flowrate and dilution system of the calibrator, and the flowrate for the AV Model BB-100 dilution system were all calibrated by use of a bubble flowmeter and a dry test meter at the beginning, midway through, and at the end of the measurement program.

3.9.1.2 Calibration of Meteorological Equipment

Calibration checks of the meteorological equipment were done on-site. The wind cups were turned to ascertain that the bearings were in normal condition. The wind vanes were aligned to the true north, true south, and true north again to calibrate the recorder output. The local magnetic north declination of +10° was accounted for. The temperature output from each station was checked daily by using an NBS traceable mercury thermometer.

3.9.1.3 Station Checks

Station checks were performed daily by AV personnel using the Daily Check List form prepared for the project. The main concerns here were to ensure that the analyzers and the supporting equipment were in proper working order.

Zero and span were checked for the analyzers during the station check. For NO/NO_x and O_3 instruments, this was accomplished by using the on-site Bendix Model 8861 or 8851, or Monitor Labs Model 8500 calibrator. For THC and CH_4, a hydrocarbon-free air cylinder and a span cylinder containing approximately 8 ppm of CH_4 in ultrapure air were used.

The zero and span values for each instrument were used to determine control limits. The control limits were a useful tool to detect early instrumental problems.

Any instrument problems were reported by the station check personnel to the Field Manager on the same day so that corrective action could be initiated as soon as possible. In addition, an instrument status report was provided weekly by the Field Manager to AV's Program Manager in Pasadena to update him with the field program status, and to enable him to provide direction when needed.

3.9.2 Airborne Measurement Program

The EPA helicopter air quality instruments, portable instrument package, and ozonesonde were involved in the measurement program. Calibration of each of the three measurement methods is described in this section.

3.9.2.1 EPA Helicopter Air Quality Instruments

The NO/NO_x and O_3 instruments were calibrated before the first flight and shortly after the last flight of a given flight day. The on-site transfer standards used were cross-referenced in EPA-Las Vegas against NBS SRM prior to the program. Multipoint calibration was performed.

3.9.2.2 Portable Instrument Package

Calibration of the portable instrument package was performed after completing each day's flights. The reference method used was O_3 GPT.

3.9.2.3 Ozonesonde

The ozonesonde used in the free balloon soundings was calibrated prior to each launch using the GPT method. In addition, an operational check was performed to ascertain that the pressure sensor was responding properly and that the zero/span was stable. Calibration of the ozonesonde used in the tethered balloon soundings was performed prior to and shortly after each sounding, also using the GPT technique. Since this ozonesonde was the same as that used for the free balloon sounding, the same operational checks were performed.

3.9.3 Audits

Quality assurance verification of the O_3 and $NO\text{-}NO_2\text{-}NO_x$ systems was performed at the EPA-EMSL facility at Research Triangle Park, North Carolina, at the start of the measurement program. The agreements for both systems were within 5%. No such verifications for THC/CH_4 were performed.

During the monitoring phase, the project was further audited by Research Triangle Institute (RTI), under contract to the EPA. Three audits were conducted for the O_3 and $NO\text{-}NO_2\text{-}NO_x$ analyzers and one audit for the THC/CH_4 analyzers at each of the five surface monitoring stations. The EPA helicopter air quality instruments, and the O_3 portable instrument package, were audited by RTI once during the measurement program. The supplemental stations were also audited by RTI. Results of these audits are documented elsewhere (Pasquini and Hackworth, 1978; Grimes and Pasquini, 1978; Pasquini and Grimes, 1978). A summary of the results is presented in Appendix A.

The acceptable criteria for all audits were set at ±15% agreement for the slope of regression analysis of the audit data, and ±0.015 ppm for the intercept. Any audit results indicating that these limits were exceeded resulted in recalibration or repair/recalibration of the instrument(s) in question as promptly as possible.

4. CHARACTERIZATION OF OZONE AND PRECURSOR TRANSPORT INTO PHILADELPHIA

This chapter presents results of the analysis of data collected in Philadelphia during the summer of 1978. Although monitoring at Sites 1 through 5 began in July, there were many operational and instrumentation problems in the first month of the program. Thus, only data collected during August and September were used for the analysis.

4.1 AVERAGE AND MAXIMUM LEVELS

Table 8 presents the average and maximum hourly averaged ozone and precursor concentrations observed at all monitoring locations during August and September. Site locations were shown in Figure 2 . Ozone levels were quite high, even at sites located predominantly upwind. Precursor concentrations were generally quite low except at downtown locations. High precursor concentrations at upwind locations were infrequent and usually not sustained, indicating a lack of significant large scale precursor transport into the study area.

Table 9 presents a frequency distribution of ozone levels observed at all sites. The greatest frequency of concentrations in excess of 0.120 ppm occurred at Ancora, located southeast of Philadelphia, while the greatest frequency of concentrations in excess of 0.080 ppm occurred at Site 3, located west of Philadelphia, predominantly upwind. The lowest frequency of concentrations in excess of 0.080 ppm occurred at the South Broad Street site in downtown Philadelphia. Sites located at Franklin Institute, Somerville, and Bivalve also recorded a relatively low frequency of ozone concentrations in excess of 0.080 ppm.

Figures 12 through 16 present ozone wind roses for all sites. These depict, simultaneously, the frequency distribution of ozone concentrations and wind direction. The wind directions associated with high ozone concentrations are easily identified

Table 8. AVERAGE AND MAXIMUM OZONE AND PRECURSOR CONCENTRATIONS (in ppm) DURING AUGUST AND SEPTEMBER.

Site	Ozone			Oxides of Nitrogen			Non-Methane Hydrocarbons		
	Peak	Average		Peak	Average		Peak	Average	
		August	September		August	September		August	September
1	0.145	0.038	0.027	0.117	0.009	0.018	1.5	0.1	0.1
2	0.129	0.026	0.024	0.102	0.017	0.019	1.9	0.2	0.3
3	0.142	0.047	0.035	0.100	0.016	0.014	1.8	0.3	0.3
4	0.166	0.038	0.034	0.095	0.010	0.016	2.1	0.1	0.1
5	0.138	0.028	0.035	0.176	0.016	0.013	2.0	0.1	0.2
So. Broad Street	0.180	0.018	0.013	0.300	0.098	0.115	-	-	-
Franklin Institute	0.250	0.023	0.018	0.370	0.071	0.082	-	-	-
Lancaster	0.122	0.034	0.024	-	-	-	-	-	-
Somerville	0.192	0.015	0.008	-	-	-	-	-	-
Ancora	0.142	0.044	0.028	-	-	-	-	-	-
Bivalve	0.120	0.037	0.031	-	-	-	-	-	-

Table 9. FREQUENCY DISTRIBUTION OF OBSERVED OZONE LEVELS (ppm) FOR AUGUST AND SEPTEMBER 1978.

Site	Total Hours Observed With Specified Ozone Concentration					
	>.120	.100-.120	.080-.099	.040-.079	.000-.040	Total
1	7	29	51	317	888	1,292
2	4	22	36	287	961	1,310
3	10	43	112	447	829	1,441
4	15	49	93	374	883	1,414
5	13	32	43	216	548	852
South Broad Street	1	1	10	133	1,256	1,401
Franklin Institute	4	13	19	184	1,178	1,398
Lancaster	1	10	34	340	837	1,222
Somerville	1	1	12	107	1,267	1,388
Ancora	22	24	53	338	817	1,254
Bivalve	0	2	31	374	998	1,405

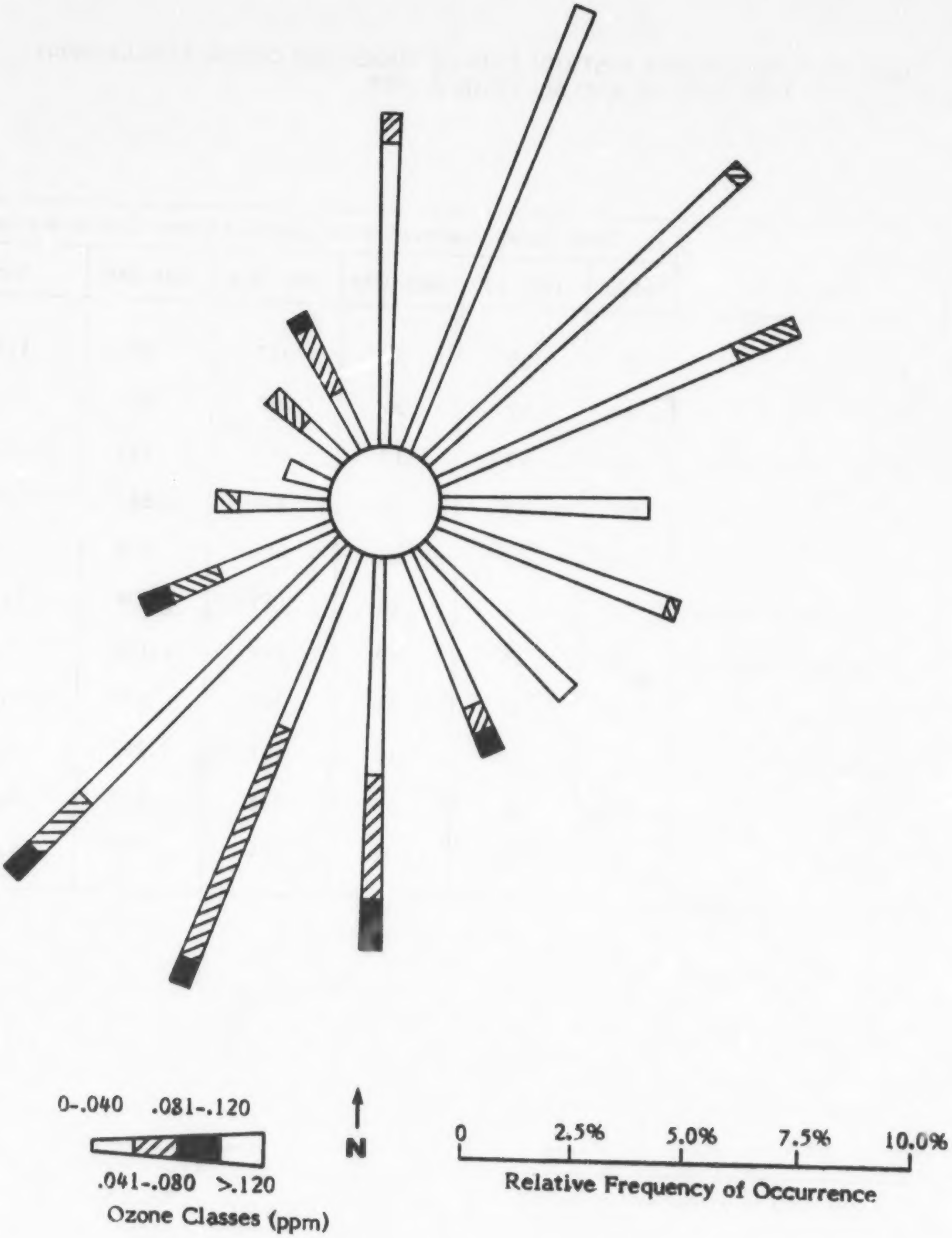

FIGURE 12. Ozone wind rose for Site 1.

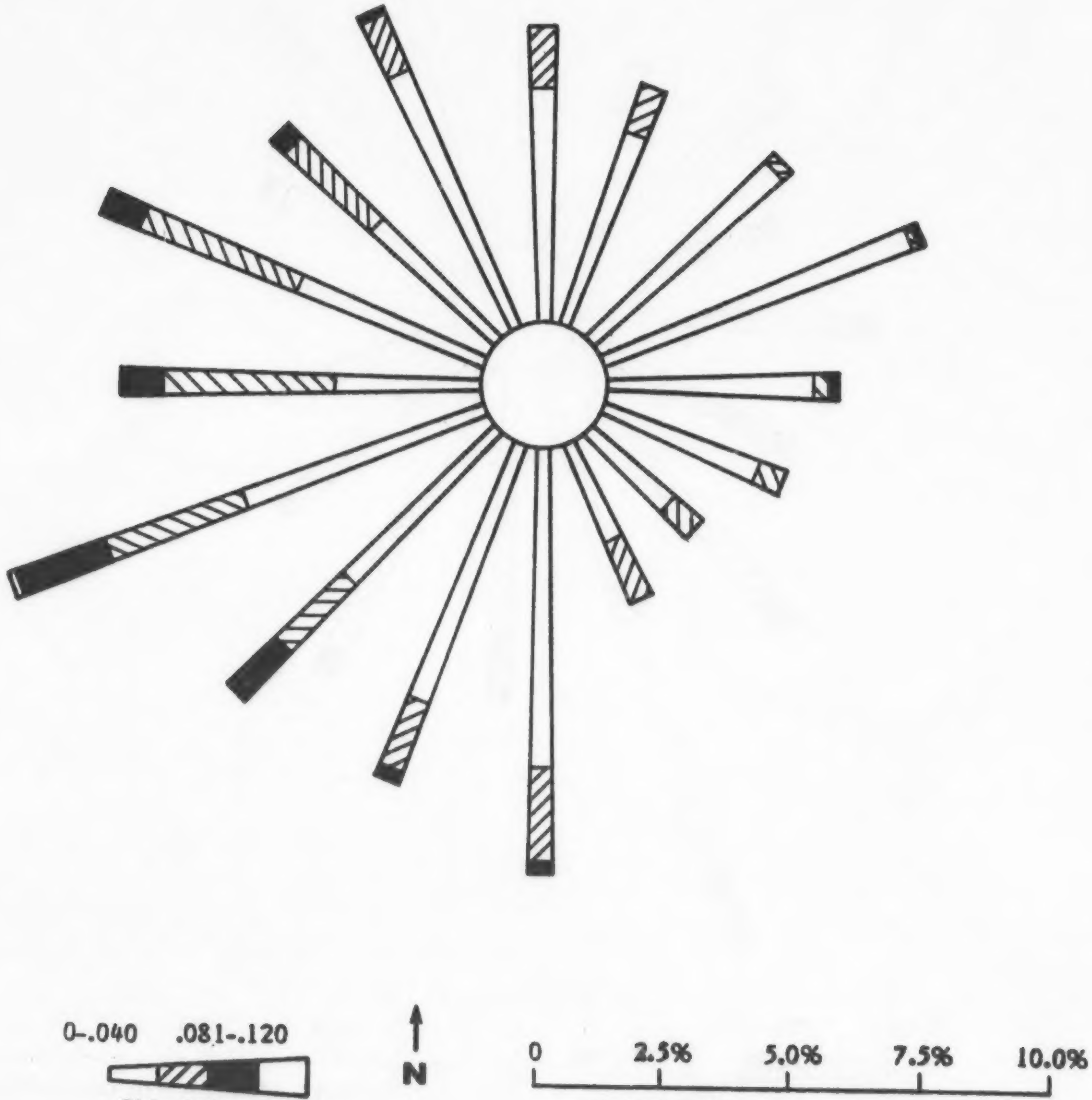

FIGURE 13. Ozone wind rose for Site 2.

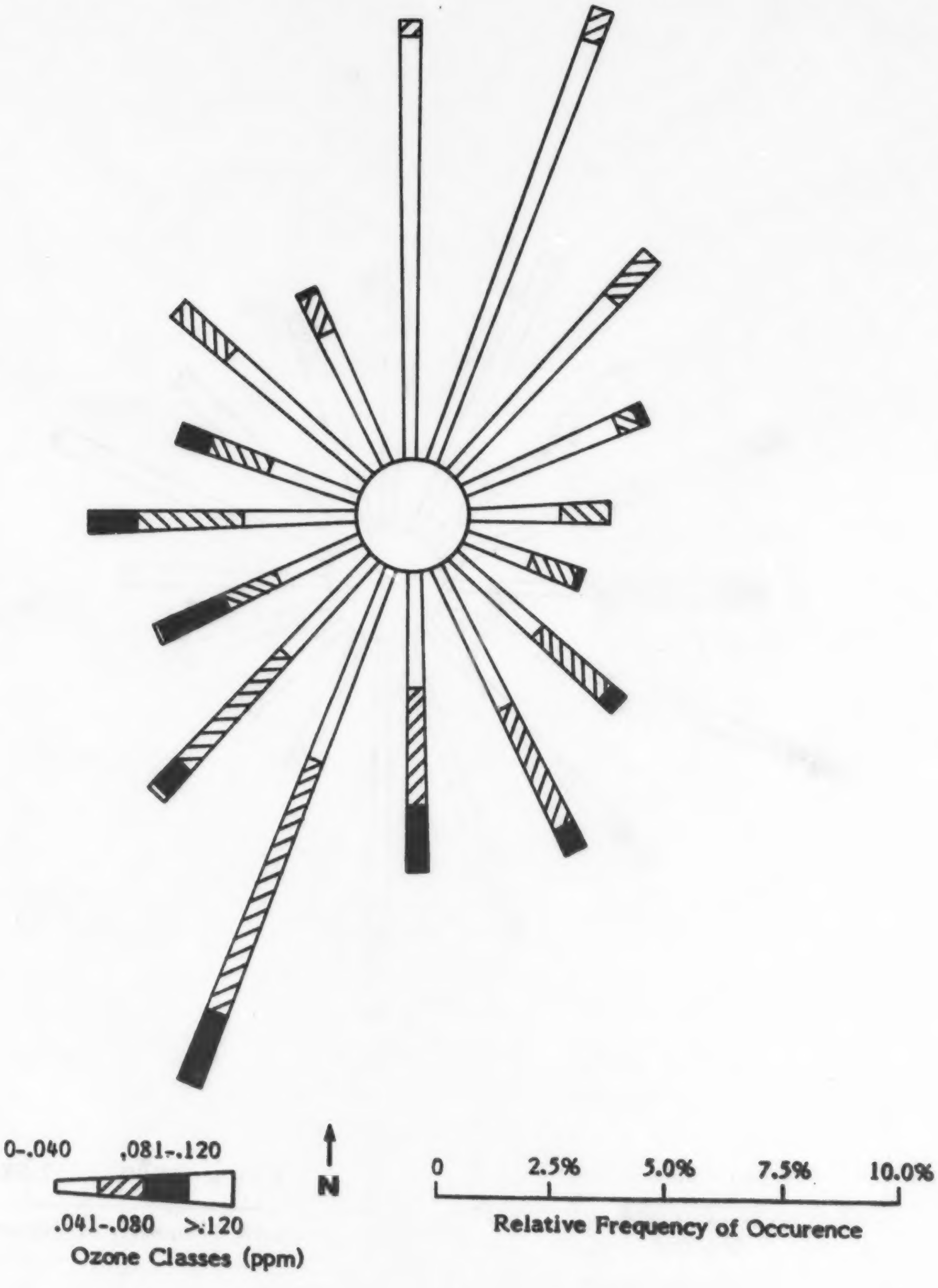

FIGURE 14. Ozone wind rose for Site 3.

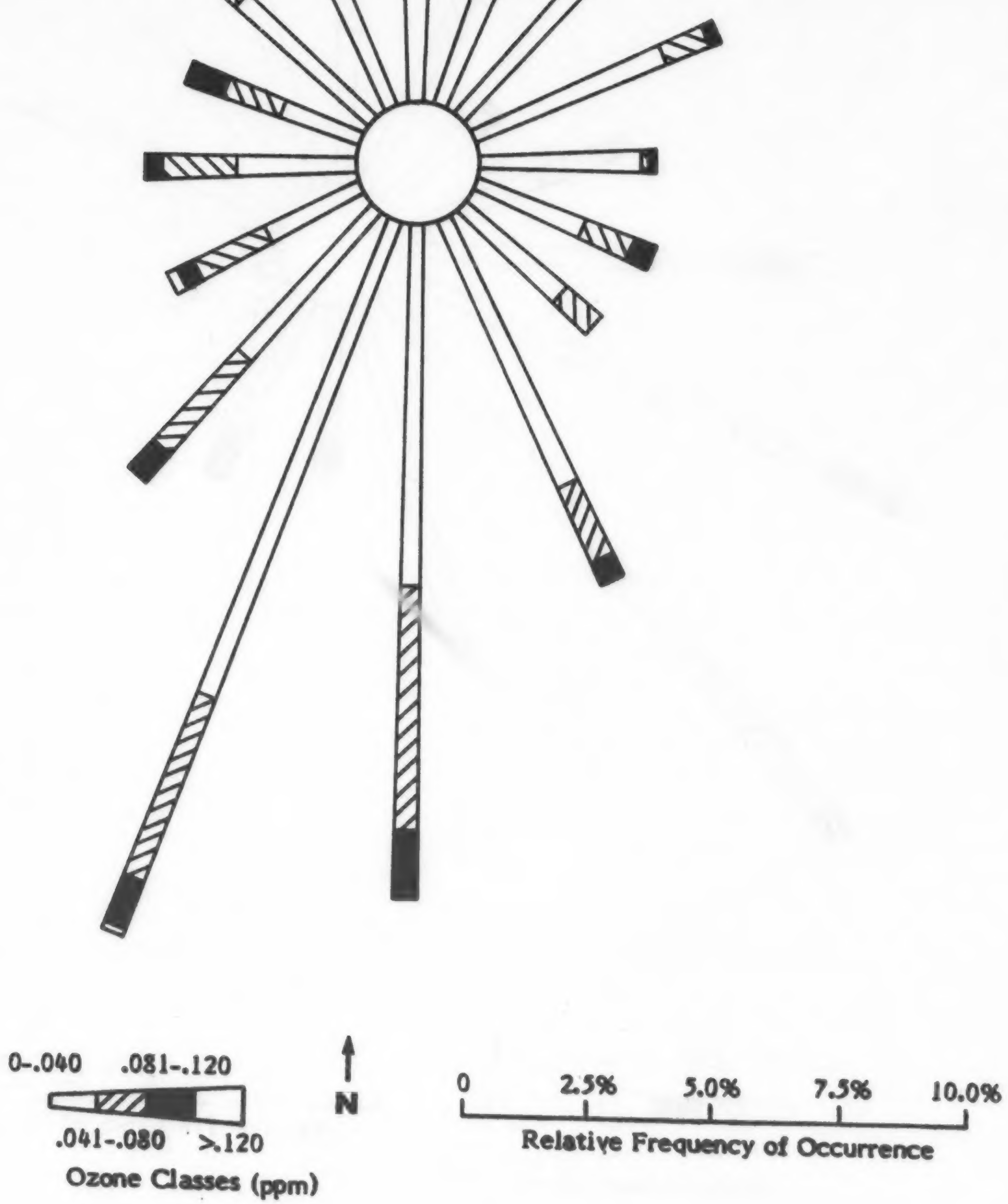

FIGURE 15. Ozone wind rose for Site 4.

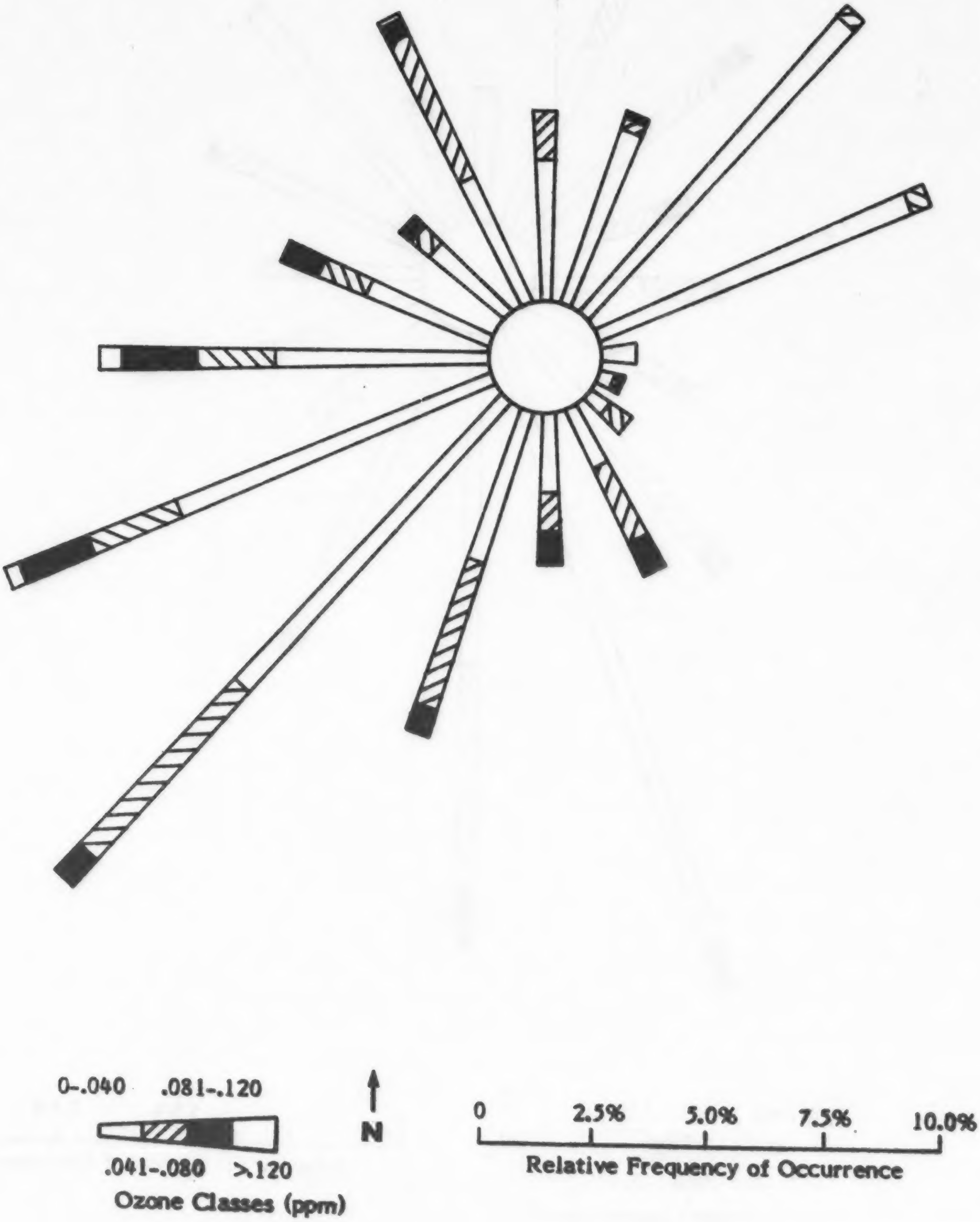

FIGURE 16. Ozone wind rose for Site 5.

from these figures. Some data are not included in Figures 12 through 16 since coincident wind direction and ozone data were not available. These data do not significantly alter the wind direction frequency distribution. An analysis of the figures shows that the most preferred wind directions for high ozone concentrations at all sites are from south to west. These directions put Sites 1, 2, and 3 upwind of Philadelphia and indicate significant transport of ozone, sometimes in excess of 0.10 ppm, from the southwest. Wind directions from north to northeast are almost never associated with high ozone concentrations, probably because these wind directions are often associated with extensive cloudiness and a resultant inhibition of photochemical activity.

4.2 TRANSPORTED LEVELS OF OZONE AND PRECURSORS

The 61 days of observation during August and September were classified into four groups of transport days based on observed ozone concentrations (especially at upwind stations) and persistence of flow (surface and aloft). The four groups and the criteria for classification are:

1. Photochemically active days with strong transport.
    a) Ozone concentrations in excess of 0.08 ppm between 1100 and 1300 EDT or 0.10 ppm later in the day at an upwind station.
    b) Prevailing flow from 180° to 315° observed at upwind stations both surface and aloft during the 24 hours prior to 1400 EDT on the day of interest.
2. Photochemically active days with weak transport.
    a) Ozone concentrations in excess of 0.08 ppm but less than 0.10 ppm at upwind stations.
    b) Prevailing flow from 180° to 315° observed at upwind stations both surface and aloft.

3. Photochemically active days with no well-defined transport.

   Ozone concentrations in excess of 0.08 ppm in the study area but not at upwind stations.

4. Days with little photochemical activity.

   No ozone concentrations in excess of 0.08 ppm observed.

Eight out of the sixty-one days were identified as photochemically active days with strong transport. The magnitude of transported ozone and precursors is suggested in Table 10 which presents ozone and precursor levels observed at the surface and aloft on the eight days during which strong transport was observed. The wind directions presented in Table 10 are prevailing wind directions at the surface between 1100 and 1700 EDT. Peak ozone levels in excess of 0.10 ppm were consistently observed at upwind sites while concentrations between 1100 and 1300 EDT and average concentrations aloft (measured by airborne instruments) were generally in excess of 0.06 ppm and sometimes in excess of 0.08 ppm. (The average concentration observed at a surface station between 1100 and 1300 EDT was suggested by U.S. EPA (1977) as an indication of the transport of ozone aloft.)

Days with strong transport were further examined and compared with other days in order to identify the peculiar characteristics of the transport situation, especially with regard to vertical profiles, horizontal gradients, and diurnal variation of ozone and precursors.

4.3 VERTICAL PROFILES

Figures 17 through 19 present vertical profiles of ozone, oxides of nitrogen, and temperature data obtained by the instrumented helicopter at Site 1 on a day with strong transport. The flight times shown indicate the beginning time of the spiral, which encompasses approximately fifteen minutes. The wind data presented in these figures were obtained by pibal tracking near the time of the helicopter spiral. Wind direction arrows point downwind. These figures typify the profiles obtained on most

Table 10. OZONE AND PRECURSOR CONCENTRATIONS (in ppm) OBSERVED DURING DAYS OF SIGNIFICANT TRANSPORT.

		Ozone				Oxides of Nitrogen		Non-Methane Hydrocarbon	
		Prevailing Wind Direction	Surface Average		Aloft Average[a]	Surface Average		Surface Average	
Date	Site	1100-1700 EDT	Maximum	1100-1300 EDT	0500 EDT	0600-0900 EDT	1100-1300 EDT	0600-0900 EDT	1100-1300 EDT
August 9	1	-	0.118	0.108	0.082	0.014	0.010	0.3	0.1
	2	W[b]	0.105	0.082	0.081	0.034	0.001	-	-
	3	-	0.119	0.089	0.081	0.010	0.007	-	-
	4	WSW	0.090	0.070	-	0.000	0.000	0.4	0.0
	5	WSW	-	-	-	-	-	-	-
	So. Broad Street	-	0.060	0.050	-	0.123	0.027	-	
	Franklin Institute	-	0.080	0.055	-	0.106	0.027	-	-
	Lancaster	-	0.074	0.054	-	-	-	-	-
	Somerville	-	0.078	0.039	-	-	-	-	-
	Ancora	-	0.124	0.079	-	-	-	-	-
	Bivalve	-	0.085	0.062	-	-	-	-	-
August 17	1	-	0.087	0.077	-	0.010	0.005	0.0	0.0
	2	WNW[b]	0.064	0.050	-	0.016	0.007	-	-
	3	-	0.089	0.069	-	0.013	0.005	0.0	0.0
	4	WNW	0.083	0.066	-	-	-	0.0	0.0
	5	-	0.071	0.057	-	-	-	0.0	0.0
	So. Broad Street	-	0.060	0.045	-	0.073	0.032	-	-
	Franklin Institute	-	0.060	-	-	0.040	-	-	-
	Lancaster	-	0.072	0.052	-	-	-	-	-
	Somerville	-	0.060	0.027	-	-	-	-	-
	Ancora	-	0.095	0.041	-	-	-	-	-
	Bivalve	-	0.080	0.050	-	-	-	-	-
August 19	1	-	-	-	0.067	0.009	-	0.6	0.3
	2	SW[b]	0.104	0.076	0.048	0.020	0.009	-	-
	3	-	0.142	0.103	0.071	-	-	0.2	0.0
	4	WSW	0.123	0.082	-	-	-	0.1	0.1
	5	WNW	0.105	0.038	-	0.002	0.003	0.0	0.0
	So. Broad Street	-	0.100	0.045	-	0.166	0.045	-	-
	Franklin Institute	-	0.110	0.055	-	0.200	0.042	-	-
	Lancaster	-	0.122	0.065	-	-	-	-	-
	Somerville	-	0.088	0.032	-	-	-	-	-
	Ancora	-	0.147	0.075	-	-	-	-	-
	Bivalve	-	0.095	0.067	-	-	-	-	-
August 22	1	-	-	-	0.070	0.029	0.008	0.1	0.0
	2	NNW[b]	0.079	0.059	0.062	0.044	0.016	0.1	0.1
	3	WSW	0.108	0.071	0.052	-	0.007	0.2	0.0
	4	NW	0.098	0.063	-	-	-	0.1	0.0
	5	NW	0.110	0.062	-	0.019	-	0.0	0.0
	So. Broad Street	-	0.060	0.045	-	0.067	0.037	-	-
	Franklin Institute	-	0.080	0.060	-	0.150	0.037	-	-
	Lancaster	-	0.085	0.044	-	-	-	-	-
	Somerville	-	0.065	0.019	-	-	-	-	-
	Ancora	-	0.142	0.083	-	-	-	-	-
	Bivalve	-	0.080	0.057	-	-	-	-	-

Table 10. (continued)

Date	Site	Ozone				Oxides of Nitrogen		Non-Methane Hydrocarbon	
		Prevailing Wind Direction	Surface Average		Aloft Average[a]	Surface Average		Surface Average	
		1100-1700 EDT	Maximum[c]	1100-1300 EDT	0500 EDT	0600-0900 EDT	1100-1300 EDT	0600-0900 EDT	1100-1300 EDT
August 23	1	-	-	-	0.070	0.020	0.020	0.0	0.0
	2	NW[b]	0.080	0.066	0.068	0.037	0.017	0.1	0.1
	3	WNW	0.108	0.079	-	0.017	0.008	0.1	0.0
	4	NW	0.101	0.079	-	-	-	0.0	0.1
	5	NNW	0.111	0.042	-	0.025	0.024	0.0	0.0
	So. Broad Street	-	0.080	0.040	-	0.120	0.045	-	-
	Franklin Institute	-	0.090	0.050	-	0.080	-	-	-
	Lancaster	-	0.101	0.052	-	-	-	-	-
	Somerville	-	0.061	0.013	-	-	-	-	-
	Ancora	-	0.139	0.084	-	-	-	-	-
	Bivalve	-	0.100	0.072	-	-	-	-	-
August 24	1	-	-	-	0.072	0.011	0.018	0.0	0.0
	2	W[b]	0.121	0.083	0.070	0.046	0.018	0.1	0.0
	3	WSW	0.133	0.109	-	-	-	0.3	0.0
	4	W	0.126	0.106	0.068	-	-	0.4	0.0
	5	W	0.111	0.088	-	0.020	0.019	0.0	0.0
	So. Broad Street	-	0.100	0.055	-	0.083	0.045	-	-
	Franklin Institute	-	0.120	0.075	-	0.070	0.027	-	-
	Lancaster	-	0.102	0.064	-	-	-	-	-
	Somerville	-	0.090	0.040	-	-	-	-	-
	Ancora	-	-	-	-	-	-	-	-
	Bivalve	-	0.055	-	-	-	-	-	-
September 6	1	-	0.086	0.079	-	0.066	-	0.2	0.1
	2	W	0.129	0.048	-	0.040	0.059	0.5	0.9
	3	SW	0.131	0.063	-	0.031	0.019	0.2	0.0
	4	-	0.145	0.101	-	0.033	-	0.1	0.3
	5	WSW	-	-	-	0.002	0.000	0.0	0.0
	So. Broad Street	-	0.070	0.015	-	0.163	-	-	-
	Franklin Institute	-	0.090	0.040	-	-	-	-	-
	Lancaster	-	0.100	0.020	-	-	-	-	-
	Somerville	-	0.078	0.020	-	-	-	-	-
	Ancora	-	0.106	0.077	-	-	-	-	-
	Bivalve	-	0.080	0.042	-	-	-	-	-
September 21	1	SSW	0.094	0.071	-	0.012	0.006	0.2	0.1
	2	WSW	0.109	0.063	-	0.035	0.018	0.2	0.3
	3	SSW	0.119	0.047	-	0.002	0.004	0.1	0.1
	4	S	0.104	0.044	-	0.017	0.014	0.1	0.1
	5	W	0.138	0.065	-	0.010	0.027	0.3	0.5
	So. Broad Street	-	0.020	0.010	-	0.176	0.080	-	-
	Franklin Institute	-	0.060	0.020	-	0.140	-	-	-
	Lancaster	-	0.093	0.029	-	-	-	-	-
	Somerville	-	0.089	0.029	-	-	-	-	-
	Ancora	-	0.069	0.045	-	-	-	-	-
	Bivalve	-	0.065	0.032	-	-	-	-	-

[a] Transport layer average observed during early morning flight by instrumented helicopter at approximately 0500 EDT. Transport layer is defined as the layer above the layer of surface ozone depletion.

[b] Wind direction obtained from nearby Wilmington Airport.

[c] Maximum for entire day.

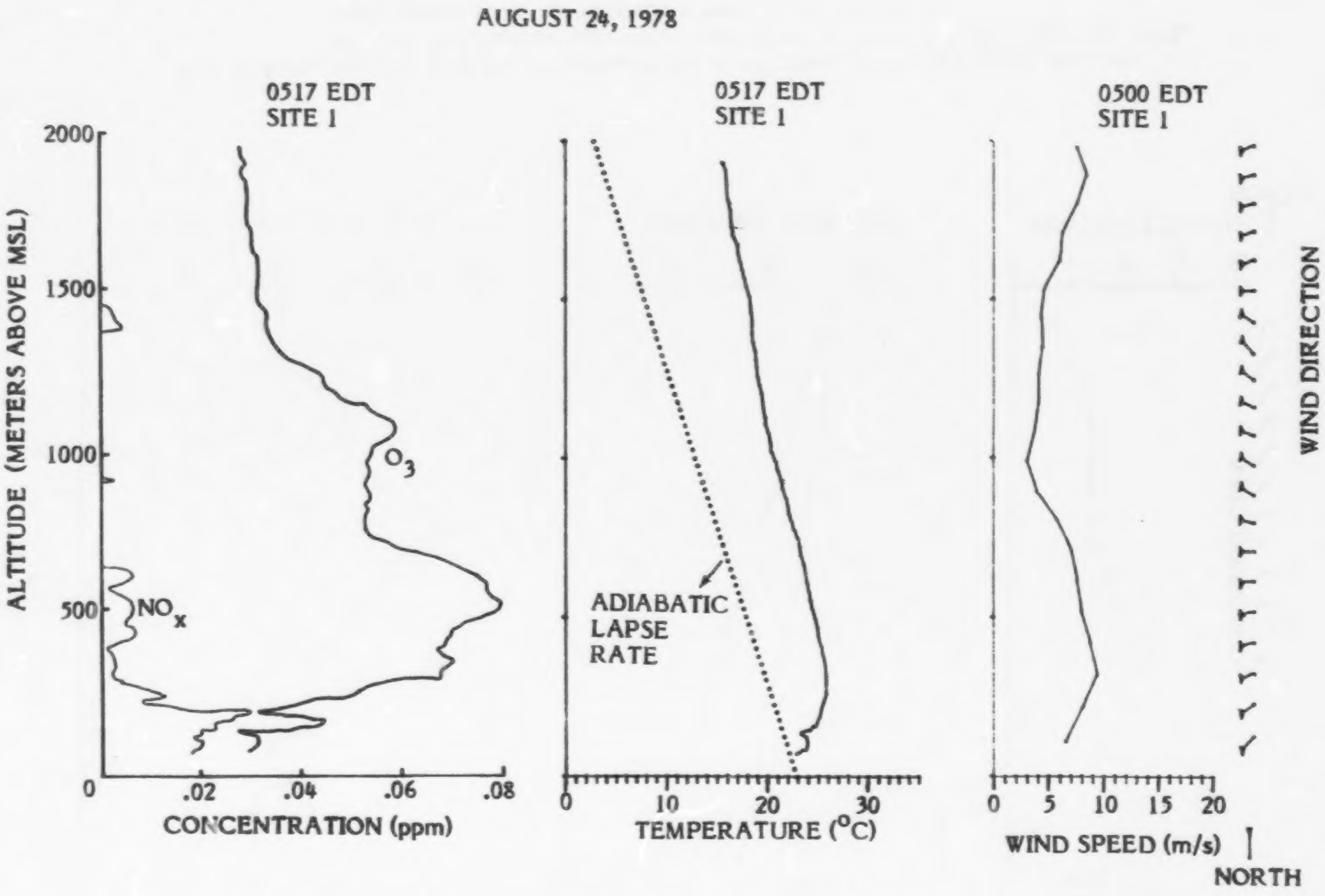

FIGURE 17. Vertical profiles of ozone, oxides of nitrogen, and temperature obtained by the instrumented helicopter over Site 1 at 0517 EDT on August 24, 1978. Also shown is the corresponding vertical wind profile.

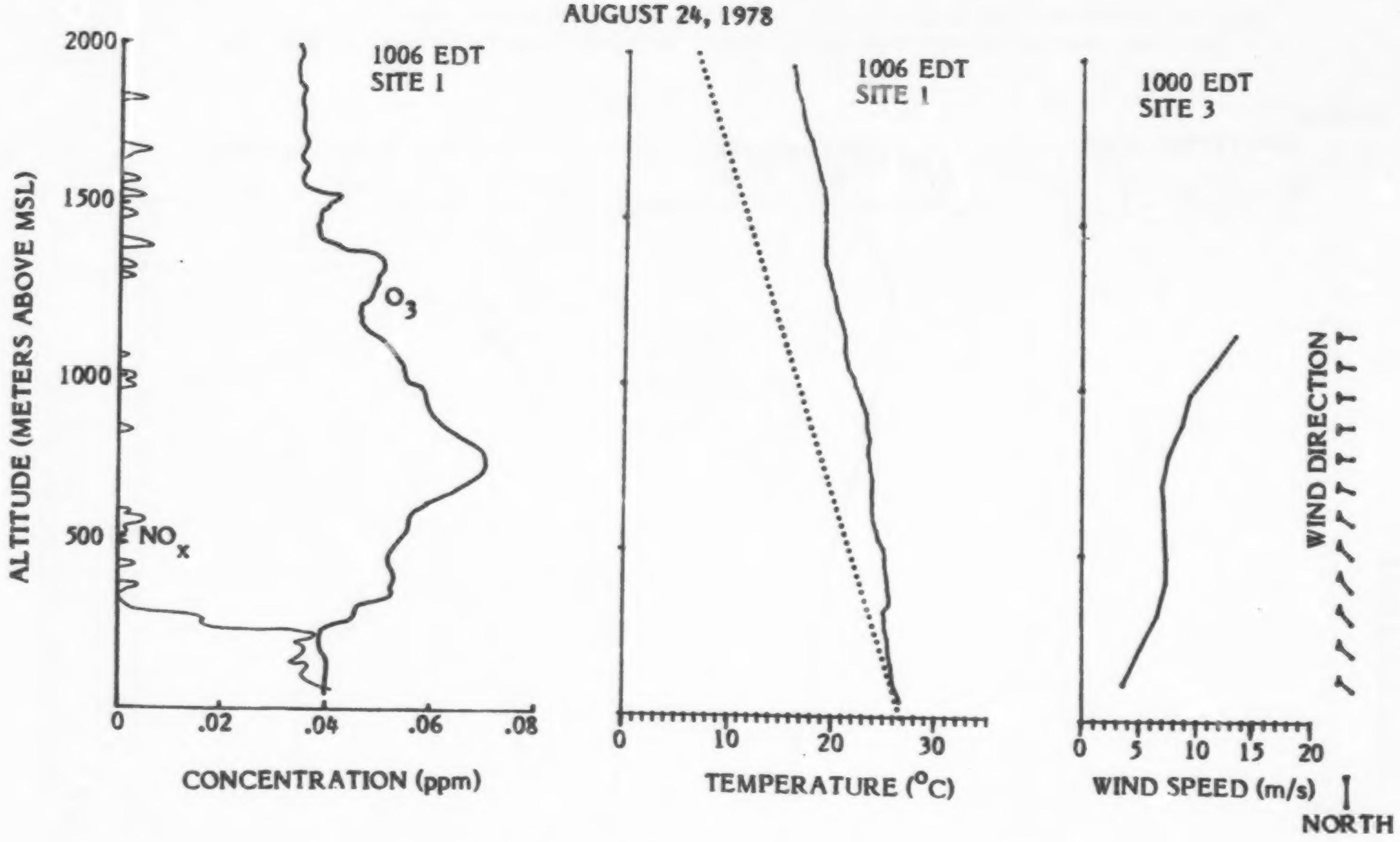

FIGURE 18. Vertical profiles of ozone,oxides of nitrogen, and temperature obtained by the instrumented helicopter over Site 1 at 1006 EDT on August 24, 1978. Also shown is the corresponding vertical wind profile.

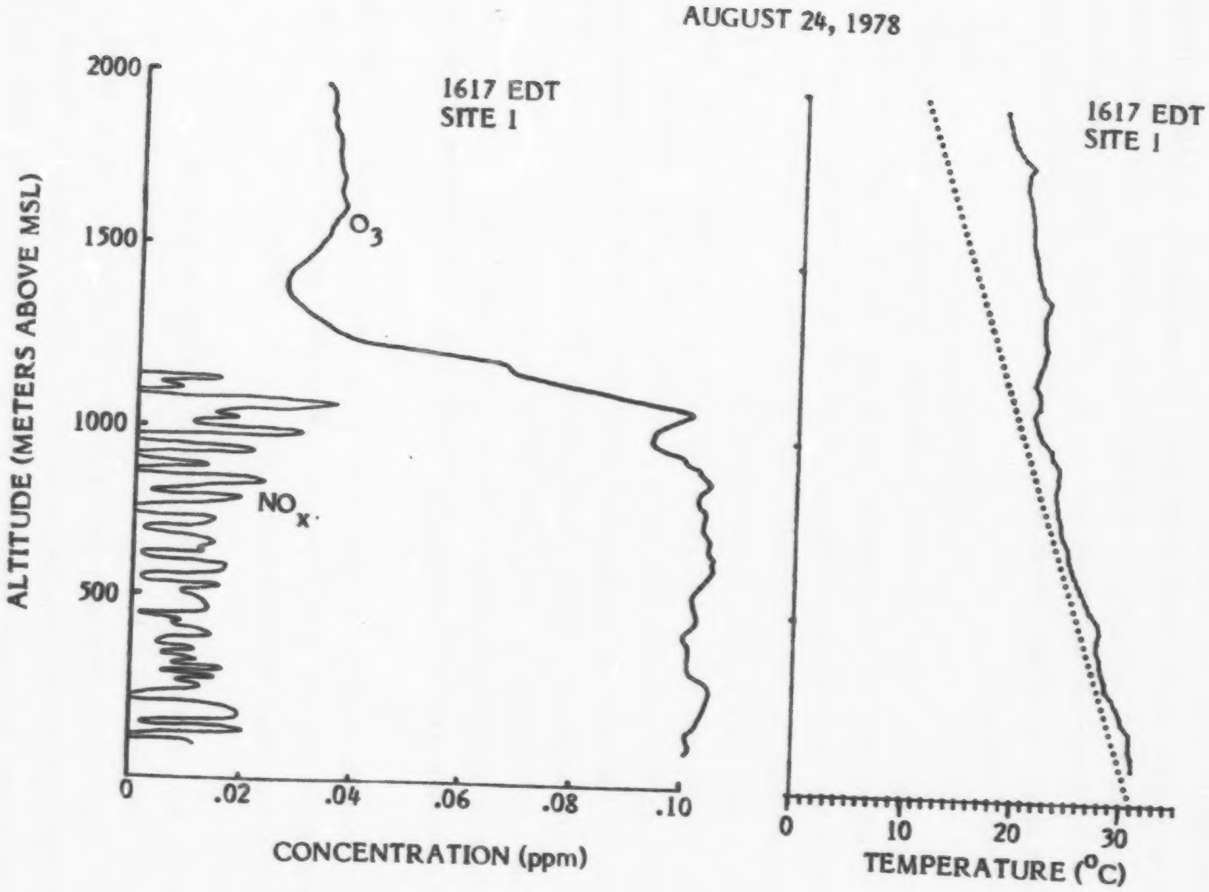

FIGURE 19. Vertical profiles of ozone, oxides of nitrogen, and temperature obtained by the instrumented helicopter at 1617 EDT over Site 1 on August 24, 1978.

transport days. During the early morning flights on this and other transport days a substantial reservoir of ozone was observed aloft with depressed ozone levels near the surface. The depressed ozone levels were often accompanied by slightly elevated concentrations of oxides of nitrogen. The late morning flights, usually made after 1000 EDT, indicate some buildup in surface ozone, although higher concentrations continue to exist aloft. In the afternoon, a nearly uniform ozone profile to the top of the mixed layer was observed.

Figure 20 presents vertical profiles of ozone, temperature, wind speed and wind direction at a site upwind of Philadelphia for a day during which photochemical activity was observed but little ozone transport into the study area was apparent. The soundings were obtained by an ozonesonde beneath a free lift balloon. The ozone reservoir aloft in the mixing layer is somewhat less than that observed on days of significant ozone transport, although the difference is not substantial. The temperature profile for both the early morning and mid-afternoon sounding indicates a limit to vertical mixing in the form of an elevated inversion at about 1,850 meters above ground level. The maximum ozone concentration observed in the early morning sounding below 1,850 meters is 0.055 ppm, which is generally less than the levels observed on days of significant transport. The wind direction is southerly at this level, a direction often associated with transport of higher levels of ozone (see Figure 12).

Another important aspect of this sounding is the appearance of high ozone concentrations above the elevated inversion. Wind flow at this level is from the southwest, a direction more often associated with ozone transport.

Figures 21 and 22 present vertical profiles of ozone and oxides of nitrogen obtained by the instrumented helicopter during a day in which photochemical activity was relatively low, due to the fact that a relatively clean air mass behind a fast moving cold front had moved into the area. The profiles indicate somewhat lower ozone concentrations than those obtained on days of significant photochemical activity. Surface depletion of ozone is still noticeable, however. It is interesting to note that concentrations near the surface in the morning hours are of the same magnitude as on transport days. Thus, until the time of mixing, surface ozone monitors contribute little or no information about ozone levels aloft.

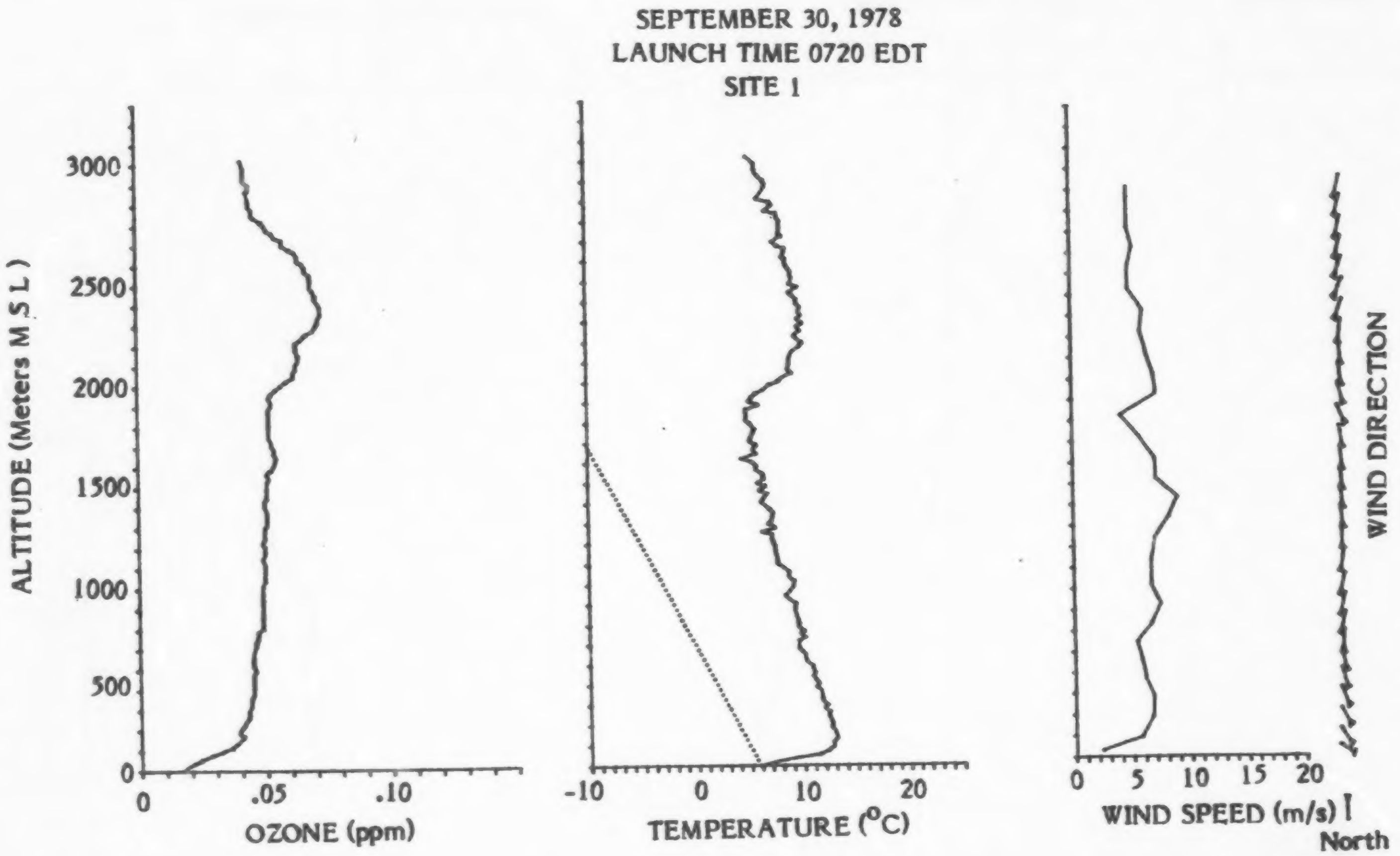
SEPTEMBER 30, 1978
LAUNCH TIME 0720 EDT
SITE 1

FIGURE 20. Vertical profiles of ozone, temperature, wind speed, and wind direction over Site 1 on a photochemically active day with little observed transport. The profiles were obtained by an ozonesonde beneath a free lift balloon on September 30, 1978.

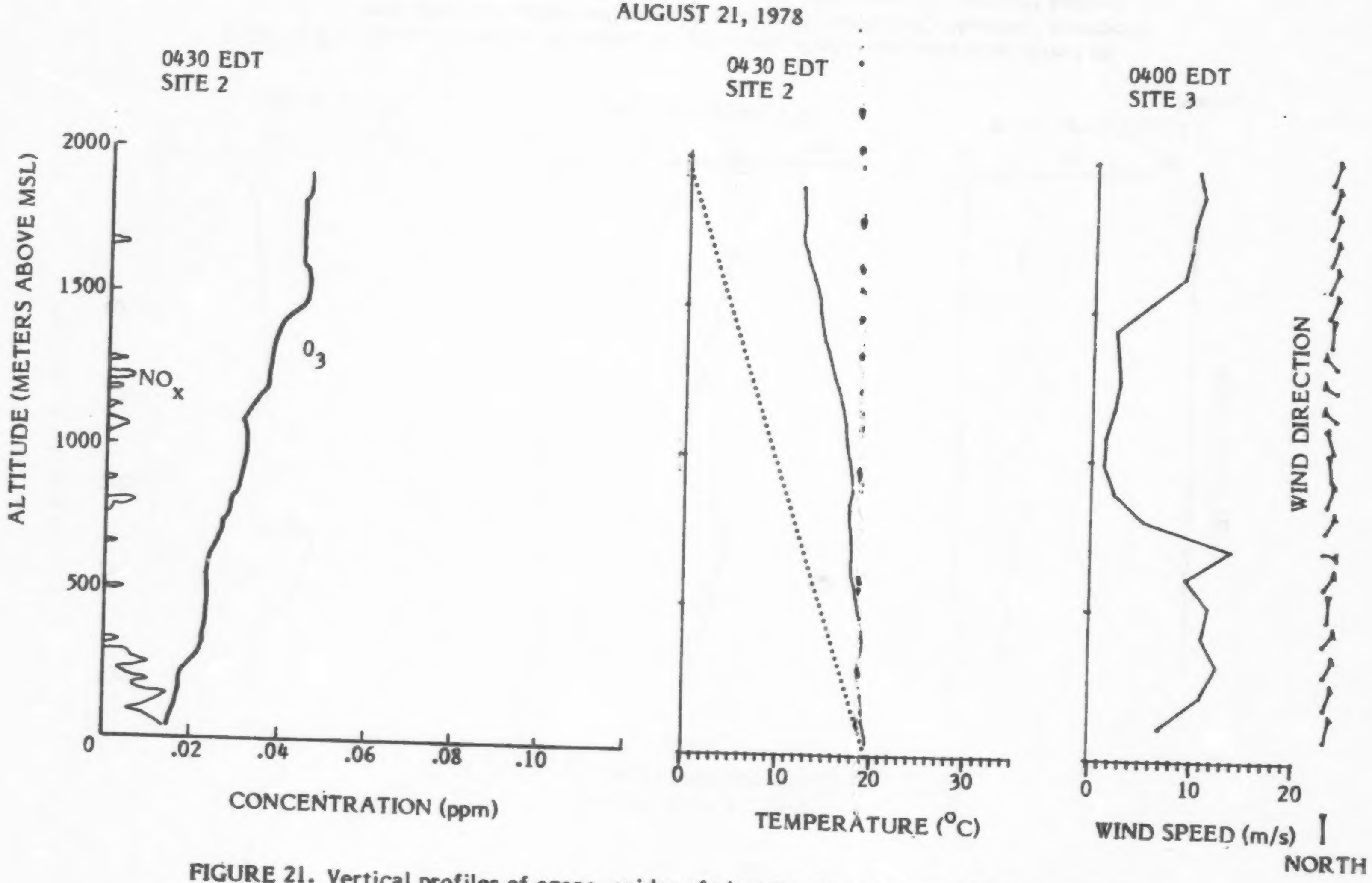

FIGURE 21. Vertical profiles of ozone, oxides of nitrogen, temperature and wind obtained by the instrumented helicopter at 0430 EDT over Site 2 on August 21, 1978.

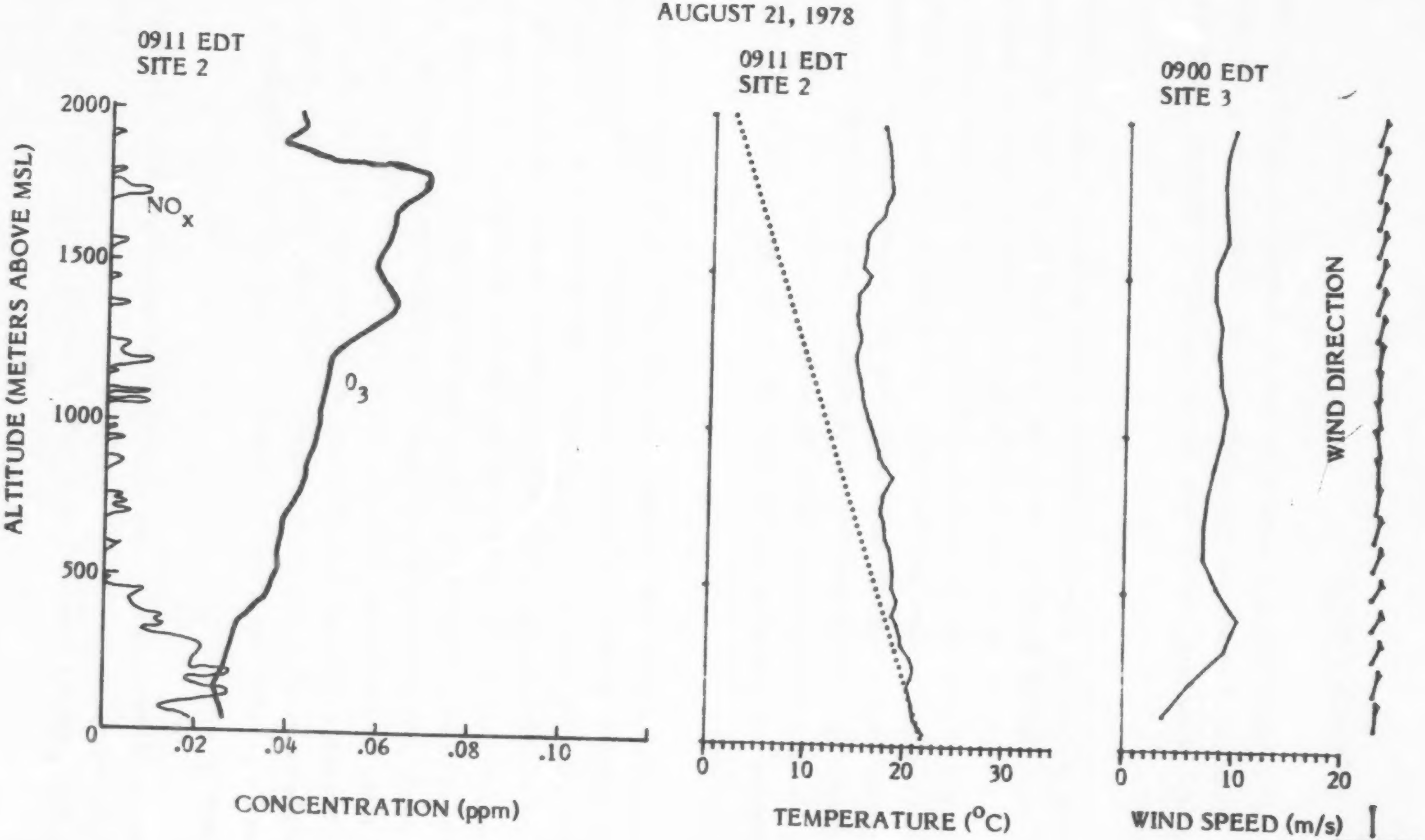

FIGURE 22. Vertical profiles of ozone, oxides of nitrogen, and temperature obtained by the instrumented helicopter at 0911 EDT over Site 2 on August 21, 1978. Also shown is the corresponding vertical wind profile.

4.4 HORIZONTAL GRADIENTS

Most of the data collected, with some notable exceptions, suggests that, while horizontal gradients of ozone and precursors exist at the surface along the upwind boundary of the study area, the features of the transported air mass are generally homogeneous.

Vertical profiles of ozone and precursors aloft obtained by the instrumented helicopter over upwind locations during the early morning on days of observed transport (August 9, 19, 22, 23, 24) and six other days were examined to determine similarities and differences. In general, while some differences were evident, the gross features of the profiles and the average concentrations aloft in the transport layer (above the layer of surface ozone depletion) were similar from one location to the next, despite some differences in sounding times. Figures 23 through 25 illustrate a group of upwind profiles obtained during the early morning hours of a transport day. The profiles are very similar despite the time span of over an hour required to perform all three soundings.

Helicopter transects were examined from site to site along the upwind boundary on days of observed transport. A typical transect between sites takes approximately 20 minutes, allowing little time for increase in photochemical activity. Table 11 presents the maximum gradients of ozone and oxides of nitrogen observed during these transects. The times shown are the beginning times of the transect. Winds presented were obtained by pibal observation at the height of the transect within an hour of the transect time. The gradients shown represent the difference between the minimum and maximum concentrations observed during the transect flight. The average absolute difference between concentrations at the beginning and end of a transect along the upwind boundary is 0.012 ppm ozone and 0.009 ppm NO_x. Ocassionally, large differences were observed along the transect. These may be attributed to point sources upwind.

Helicopter transects from upwind areas to primary source areas near downtown Philadelphia were examined on these same five days of observed transport. Table 12 presents the gradients observed along these transects. Most of these were flown

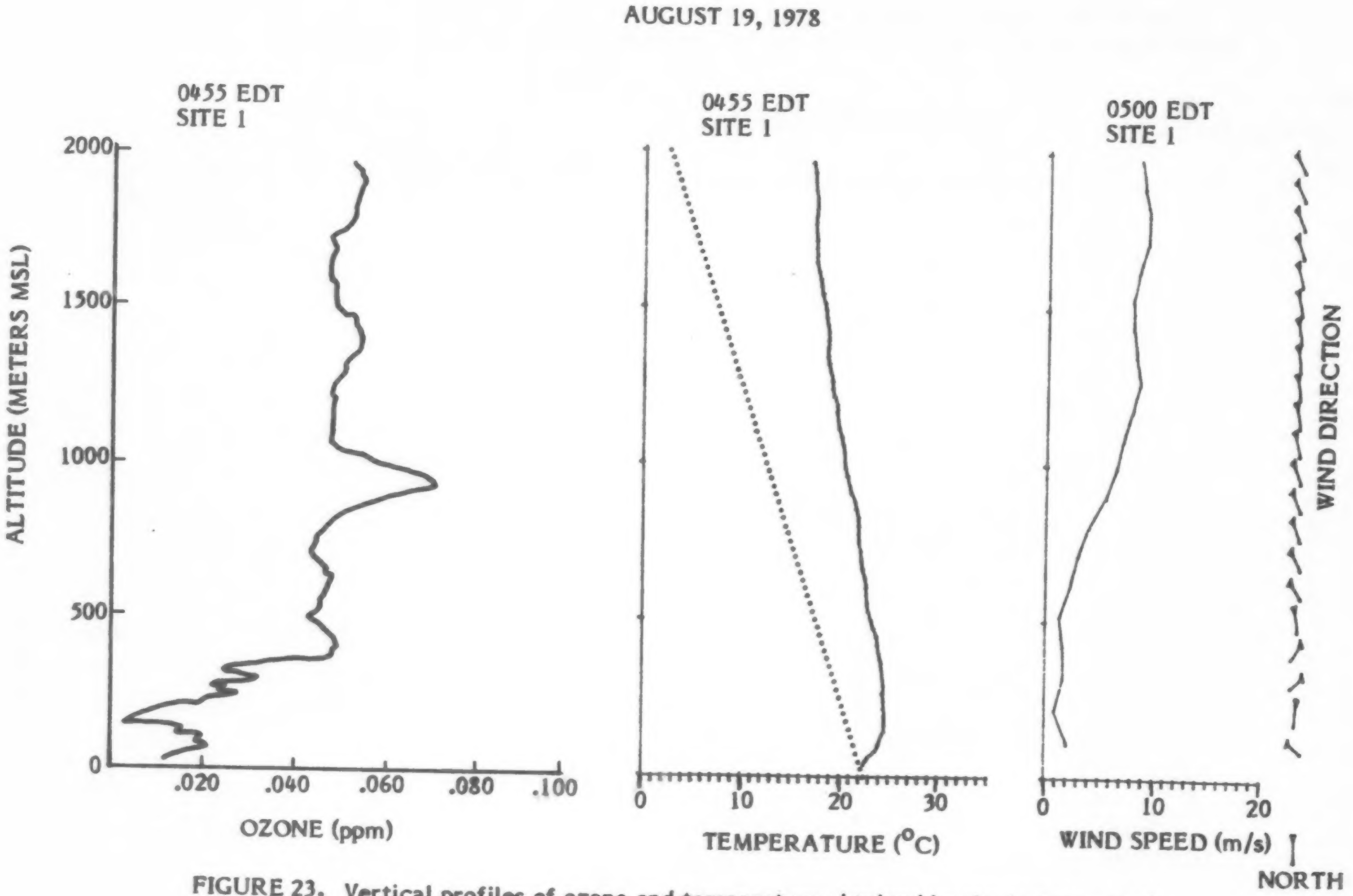

FIGURE 23. Vertical profiles of ozone and temperature obtained by the instrumented helicopter over Site 1 at 0455 EDT on August 19, 1978. Also shown is the corresponding vertical wind profile.

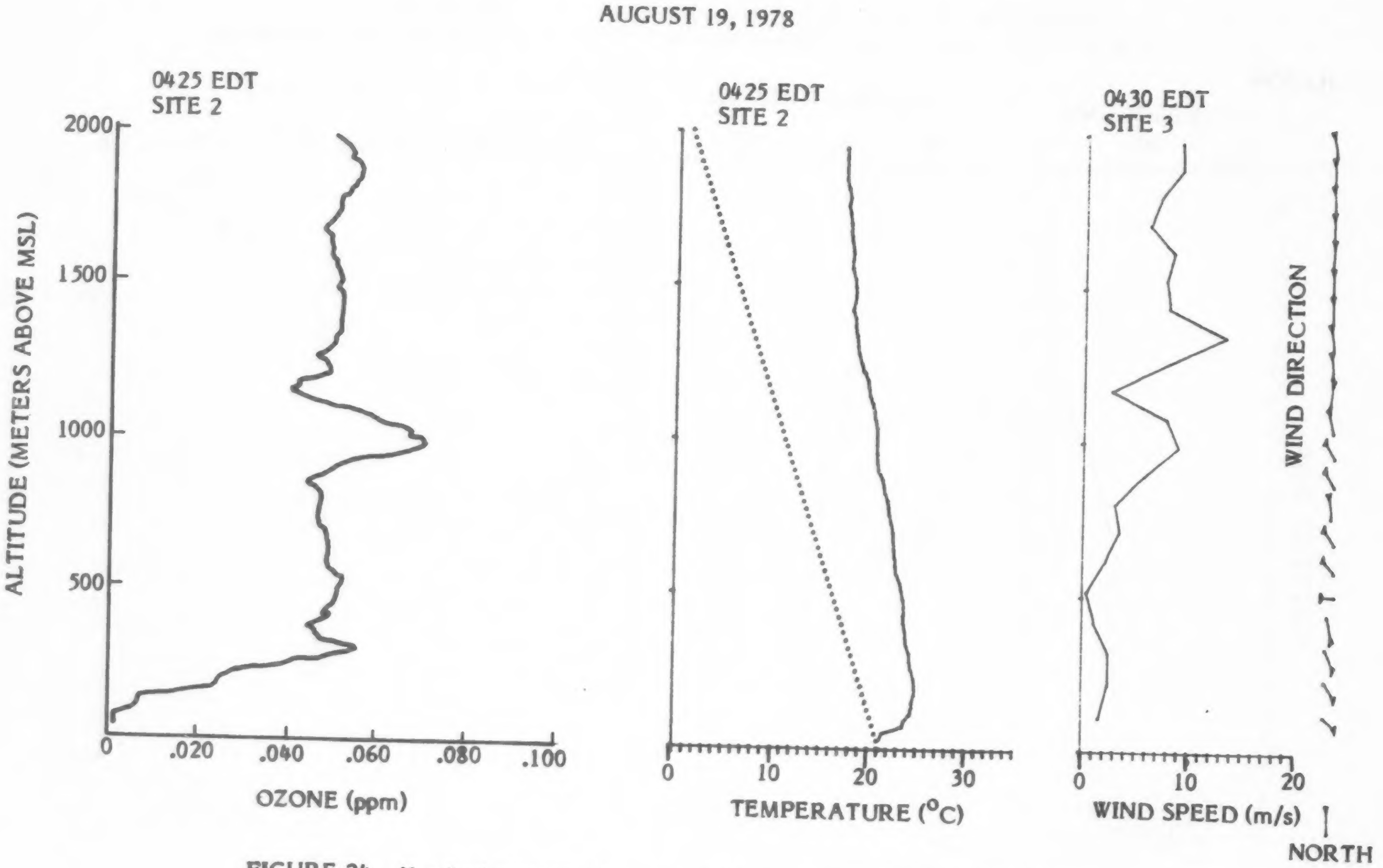

FIGURE 24. Vertical profiles of ozone and temperature obtained by the instrumented helicopter over Site 2 at 0425 EDT on August 19, 1978. Also shown is the corresponding vertical wind profile.

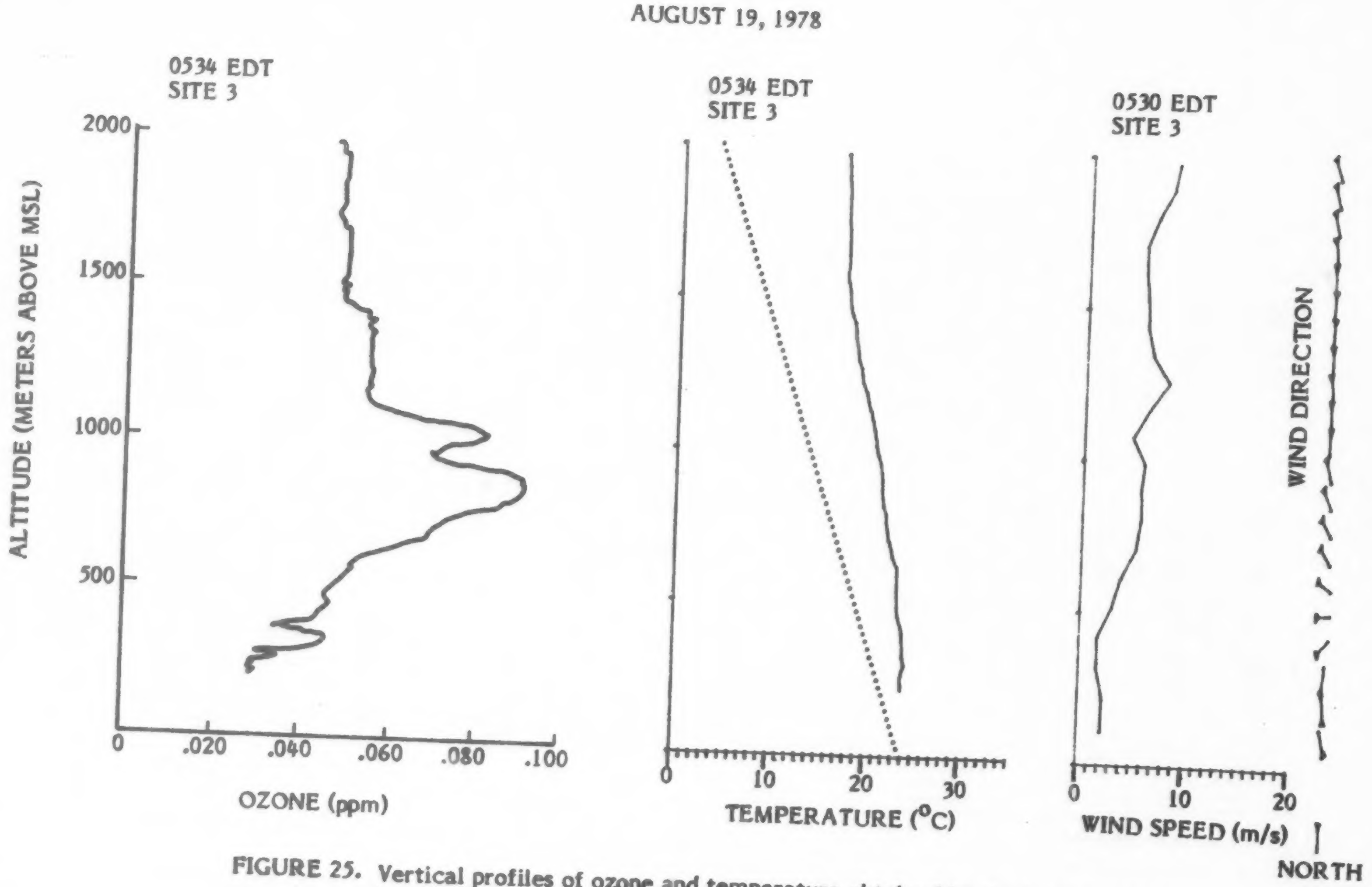

FIGURE 25. Vertical profiles of ozone and temperature obtained by the instrumented helicopter over Site 3 at 0534 EDT on August 19, 1978. Also shown is the corresponding vertical wind profile.

Table 11. GRADIENTS OF OZONE AND OXIDES OF NITROGEN OBSERVED ALOFT ALONG THE STUDY AREA UPWIND BOUNDARY.

Date	Transect Between Locations[a]	Altitude (meters m.s.l.)	Start Time (EDT)	Winds Aloft				Ozone Concentration Aloft (ppm)				NO_x Concentration Aloft (ppm)			
				Site 1		Site 3									
				WS (m/s)	WD (degrees)	WS (m/s)	WD (degrees)	Transect Start	Transect End	Absolute Difference	Maximum Absolute Difference Along Transect	Transect Start	Transect End	Absolute Difference	Maximum Absolute Difference Along Transect
8/9	2-1	610	0528	5.9	290	6.2	300	.078	.084	.006	.007	.000	.001	.001	.016
	1-3	600	0553	5.0	300	6.0	310	.078	.084	.006	.031	.000	.008	.008	.022
	W-1	910	0912	3.7	300	8.3	320	.063	.081	.018	.030	.002	.021	.019	.044
	1-3	610	0942	3.7	300	6.7	310	.091	.086	.005	.064	.005	.023	.018	.184
8/19	2-1	910	0443	5.5	320	5.7	310	.063	.041	.022	.028	.000	.006	.006	.012
	1-3	910	0511	5.5	320	5.9	320	.046	.075	.029	.035	.005	.000	.005	.013
	W-1	760	0941	7.0	280	4.4	320	.106	.092	.014	.048	.003	.004	.001	.087
	1-3	550	1018	-	-	3.9	310	.088	.061	.027	.056	.019	.081	.062	.080
8/22	2-1	340	0451	3.4	250	3.2	250	.065	.062	.003	.044	.001	.005	.004	.055
	1-3	460	0523	1.7	250	3.3	250	.076	.044	.032	.056	.006	.007	.001	.053
	3-W	240	0604	3.0	290	3.2	270	.054	.063	.009	.024	.011	.004	.007	.015
	W-1	1070	0937	1.7	200	4.6	270	.077	.076	.001	.006	.007	.009	.002	.016
	1-3	610	1016	3.2	260	2.8	270	.084	.068	.016	.021	.011	.010	.001	.032
8/23	2-1	580	0516	2.4	290	2.3	340	.065	.070	.005	.008	.007	.005	.002	.011
	2-4	500	1014	5.7	300	4.5	330	.072	.080	.008	.018	.002	.002	.000	.014
8/24	2-1	490	0504	8.0	260	6.8	280	.078	.080	.002	.016	.002	.004	.002	.008
	1-4	500	0532	6.8	270	7.0	280	.073	.076	.003	.040	.008	.003	.005	.010
	4-W	490	0614	8.1	270	8.4	270	.062	.082	.020	.056	.039	.002	.037	.096
	W-1	610	0952	6.9	250	7.2	290	.064	.064	.000	.012	.003	.009	.006	.013
	1-4	610	1022	6.9	250	9.5	280	.056	.072	.016	.026	.002	.004	.002	.023
	1-W	270	1633	-	-	-	-	.105	.098	.007	.010	.029	.022	.007	.029
Average								-	-	.012	.030	-	-	.009	.040

[a] W = Wilmington Airport

Table 12. OZONE AND GRADIENTS OF OXIDES OF NITROGEN OBSERVED ALOFT ALONG TRANSECTS FROM UPWIND AREAS TO PRIMARY SOURCE AREAS.

Date	Transect Between Locations[a]	Altitude (meters MSL)	Start Time (EDT)	Winds Aloft				Ozone Concentration Aloft (ppm)				NO_x Concentration Aloft (ppm)			
				Site 1		Site 3									
				WS (m/s)	WD (degrees)	WS (m/s)	WD (degrees)	Upwind	Down-town	Absolute Differ-ence	Maximum Absolute Difference Along Transect	Upwind	Down-town	Absolute Differ-ence	Maximum Absolute Difference Along Transect
8/9	3-6	610	1023	-	-	7.9	310	.077	.088	.011	.024	.040	.000	.040	.054
	6-W	610	1103	-	-	5.6	310	.089	.095	.006	.010	.028	.015	.013	.048
8/19	3-6	550	1018	-	-	3.9	310	.088	.061	.027	.056	.019	.081	.062	.080
8/22	3-6	610	1056	-	-	2.5	310	.069	.089	.020	.022	.007	.016	.009	.029
	6-W	150	1141	-	-	1.2	320	.091	.098	.007	.035	.041	.027	.014	.045
8/23	1-6	610	0548	6.2	280	5.0	320	.074	.065	.009	.024	.004	.000	.004	.013
	6-W	380	0631	6.0	280	7.2	310	.076	.077	.001	.008	.004	.008	.004	.014
	4-6	610	1053	-	-	7.1	330	.073	.079	.006	.021	.019	.043	.024	.047
	6-W	300	1132	-	-	5.6	330	.103	.088	.015	.027	.018	.025	.007	.049
8/24	4-6	610	1106	-	-	7.8	290	.071	.067	.004	.017	.007	.043	.036	.043
	6-W	610	1204	-	-	10.9	280	.073	.085	.012	.014	.019	.025	.006	.023
Average								.080	.081	.011	.023	.019	.027	.020	.040

[a] W = Wilmington Airport

during the late morning hours. Table 12 indicates that average ozone concentrations at the transect level over upwind areas were nearly identical to those over downtown locations while NO_x levels were only slightly lower at upwind locations. The average absolute difference between concentrations observed aloft along the upwind boundary and those observed downtown was 0.011 ppm for ozone and 0.020 ppm for NO_x with somewhat higher differences observed along the transect.

While horizontal gradients aloft may be generally minor, substantial gradients exist at ground level along the upwind study area boundary. Table 13 presents concentrations of ozone, oxides of nitrogen, and non-methane hydrocarbon (NMHC) at 0600, 0900, and 1200 EDT along the upwind boundary on days of observed transport. Ozone gradients of 0.030 ppm are common while precursors, although at low concentrations, also exhibit substantial differences. The differences in ozone and precursor concentrations observed at surface stations are probably due to differences in source strengths of ozone scavengers and precursors upwind and in the vicinity of the surface monitoring stations.

4.5 DIURNAL VARIATIONS

Diurnal variations at all sites are similar on days of strong observed transport of ozone into the study area and differ signficantly from diurnal variations on other days, especially between sites upwind and downwind of Philadelphia.

Figure 26 shows the diurnal variation of ozone at three sites on a day with strong observed transport. The diurnal variation and levels observed at other upwind sites (2 and 4) were nearly identical to Site 3. This figure shows essentially no difference between Site 3 (upwind boundary) and Site 5 (downwind boundary). It should be noted that the flow on August 24 (west to west-southwest) may not have placed Site 5 in the path of the Philadelphia plume. The downtown (South Broad Street) site shows roughly the same variation with slightly depressed values. The consistency of the diurnal variation over the study area indicates that the mechanisms of ozone formation and transport are large enough in scale to mask the effects of individual source areas. However, the effect of a Philadelphia ozone plume probably was not recorded by any of the sites, since most of the stations were concentrated in the upwind areas.

Table 13. CONCENTRATIONS OF OZONE AND PRECURSORS (in ppm) OBSERVED ALONG THE STUDY AREA UPWIND BOUNDARY AT THE SURFACE ON DAYS OF STRONG TRANSPORT.

Date	Time (EDT)	Ozone						Oxides of Nitrogen				Non-Methane Hydrocarbon			
		Site 1	Site 2	Site 3	Site 4	Lancaster	Bivalve	Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
August 9	0600	.006	.012	.038	.000	.000	.010	.013	.010	.012	.000	0.3	M	0.4	0.4
	0900	.066	.045	.053	.032	.004	.015	.020	.005	.013	.000	0.2	M	0.3	0.3
	1200	.112	.070	.099	.072	.066	.020	.005	.000	.006	.000	M	M	0.0	0.0
August 17	0600	.027	.004	.020	.014	M	.025	.000	.013	.008	M	0.0	M	0.0	0.0
	0900	.032	.028	.043	.038	M	.025	.046	.014	.012	M	0.0	M	0.0	0.0
	1200	.079	.051	M	.068	.052	.055	.004	.007	M	M	0.0	M	0.0	0.0
August 19	0600	.001	.000	.013	.000	.000	.025	.000	.013	M	M	0.0	M	0.0	0.0
	0900	.048	.018	.034	.023	.066	.020	.007	.022	M	M	0.6	M	0.1	0.1
	1200	M	.070	.104	.096	.076	.075	M	.010	M	M	0.1	M	0.0	0.0
August 22	0600	M	.000	.007	.000	.001	.025	.008	.021	.071	M	0.0	0.1	0.2	0.1
	0900	M	.022	.048	.018	.003	.015	.036	.026	.025	M	0.0	0.1	0.0	0.1
	1200	M	.058	.072	.070	.057	.060	.007	.016	.006	M	0.0	0.0	M	M
August 23	0600	M	.007	.041	.000		.040	.017	.021	.022	M	0.0	0.2	1.0	0.9
	0900	M	.033	.067	.038	.009	.040	.044	.030	.012	M	0.0	0.1	0.1	0.2
	1200	M	.059	.082	.084	.064	.075	.014	.015	.007	M	0.0	0.1	0.0	0.0
August 24	0600	M	.010	.039	M	M	M	.011	.026	M	M	0.0	0.1	0.4	0.4
	0900	M	.044	.065	.024	.002	M	.016	.017	M	M	0.0	0.0	0.1	0.2
	1200	M	.090	.115	.118	.080	M	.013	.018	M	M	0.0	0.0	0.0	0.0
September 6	0600	.000	.000	.020	.000	.000	.030	.028	.019	.017	.028	0.1	0.4	0.1	0.1
	0900	.021	.010	.018	.020	.000	.020	M	.059	.046	.025	0.8	0.7	0.1	0.0
	1200	.086	.045	.075	.078	.018	.055	M	M	.014	M	0.2	0.8	0.3	0.3
September 21	0600	.016	.012	.035	.025	.009	.040	.014	.023	.000	.007	0.2	0.2	0.2	0.1
	0900	.027	.018	.038	.023	.004	.045	.014	.022	.004	.023	0.1	0.4	0.2	0.1
	1200	.075	.068	.050	.048	.035	.060	.005	.015	.004	.017	0.1	0.3	0.1	0.0

M = Missing Data

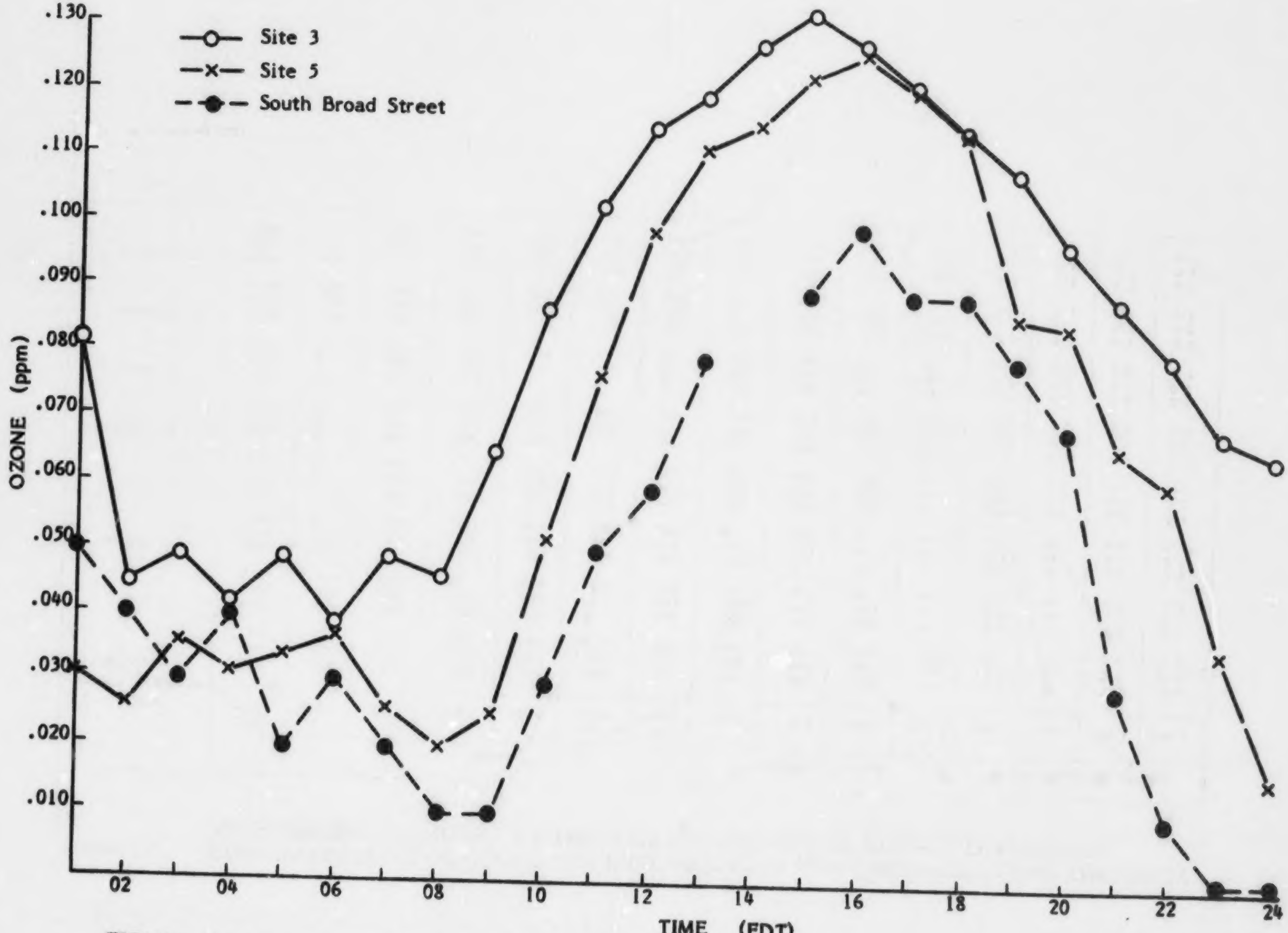

FIGURE 26. Diurnal variation of ozone at Sites 3 and 5 and the South Broad Street Site on a day of strong observed transport (August 24, 1978).

The diurnal variation of ozone at the South Broad Street Site on August 24 corresponds to the variation in NO levels. A decrease in NO levels from 0900 EDT to 1100 EDT is accompanied by the observed increase in ozone concentrations. No such direct relationship existed at Sites 3 and 5 on this day since both sites recorded low NO levels (less than 0.01 ppm) all day long. Acoustic radar measurement of mixing height at Site 1 shows a continuous increase in the depth of the surface mixed layer from 30 m at 0800 EDT to greater than 1,000 meters by 1100 EDT. This period of inversion disintegration corresponds closely to the period of rapid ozone increase at all three sites shown. Average ozone concentration aloft, as measured by the instrumented helicopter was 0.07 ppm, a level reached at upwind stations during the period of inversion breakup.

Figure 27 presents the diurnal variation of ozone at the surface on a photochemically active day with weak transport of ozone or precursors into the study area. Prevailing wind direction was southeasterly making Site 1 representative of concentrations on the upwind side of the study area. A supplemental site at Ancora, New Jersey showed a similar profile. Also shown are concentrations for the South Broad Street Site and Site 4, which was downwind of Philadelphia on this day. Comparing this with Figure 26, it is apparent that levels upwind and downtown are much depressed without the benefit of transport, while the concentration at Site 4 is of the magnitude of concentrations observed at upwind stations on transport days.

The diurnal variation of ozone during a day of little photochemical activity is illustrated in Figure 28. It differs from the transport day shown in Figure 27 primarily in the magnitude of the peak concentrations. The time of the peak is still rather late in the afternoon. Other days of this type show great variability in the time of the peak.

Table 14 presents examples of ozone peak times on three types of days: days with strong transport, days with (relatively) no transport, and days with little photochemical activity. In general, ozone maxima seem to occur later in the day in cases of strong transport, although the limited sample size and existence of several exceptions prevent generalization of this observation.

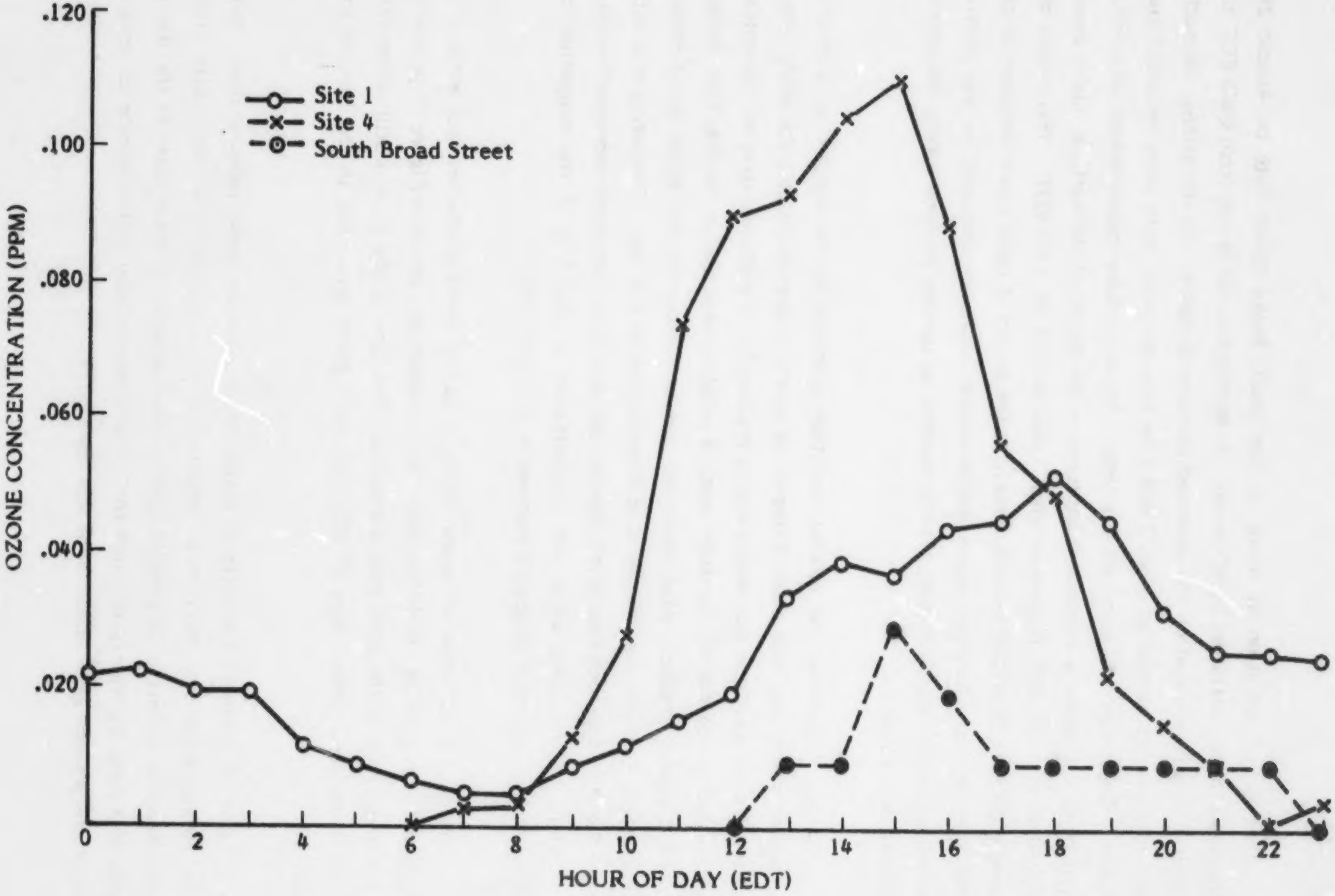

FIGURE 27. Diurnal variation of ozone at Sites 1 and 4 and the South Broad Street Site on a day of observed photochemical activity but low transported levels of ozone into the study area (August 2).

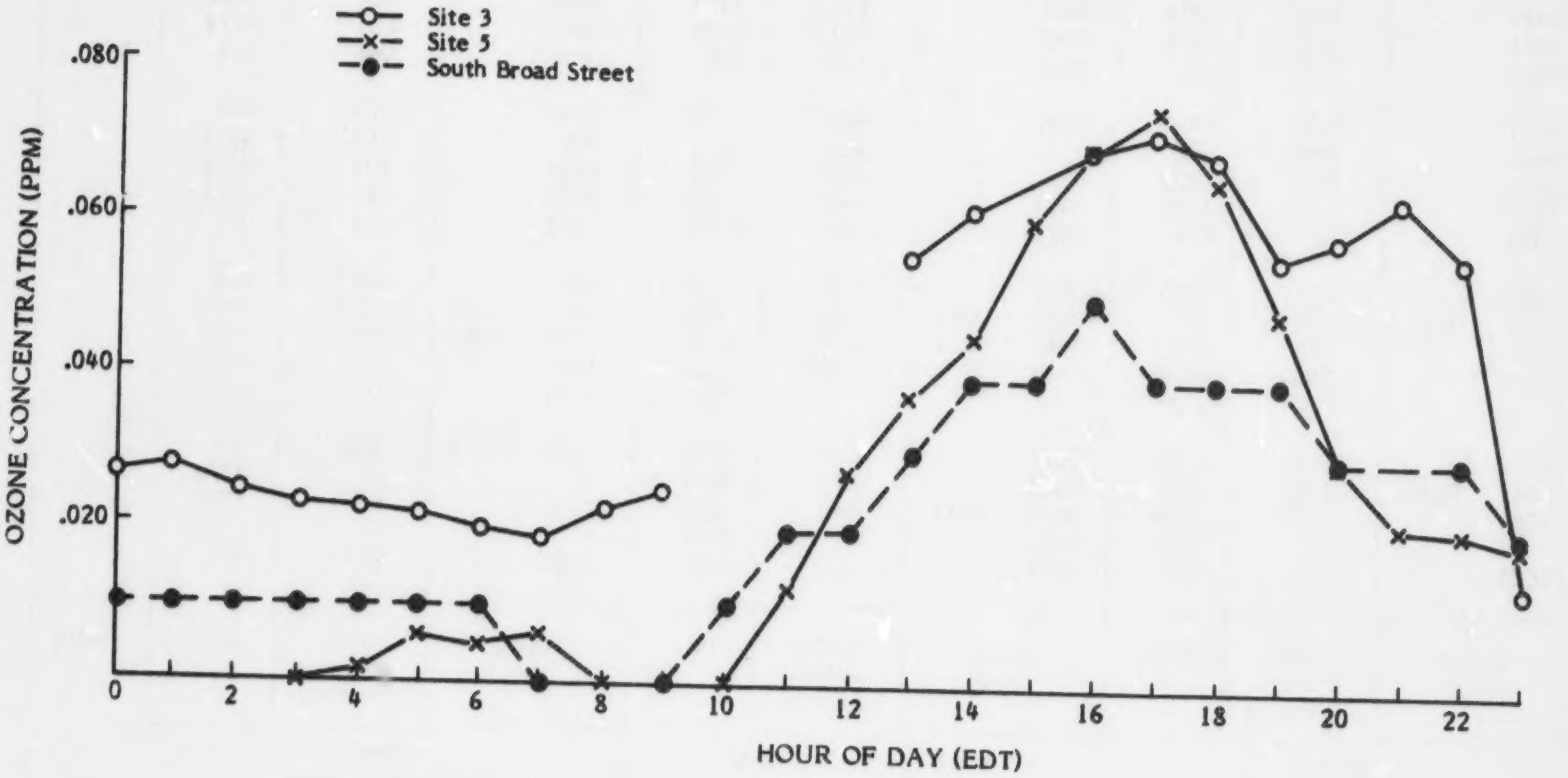

FIGURE 28. Diurnal variation of ozone at Sites 3 and 5 and the South Broad Street Site on a day of little observed photochemical activity (August 21, 1978).

Table 14. TIMES (EDT) OF MAXIMUM OZONE CONCENTRATION.

Site	Photochemically Active Days with Strong Transport			Photochemically Active Days with No Well-Defined Transport			Days with Little Photochemical Activity		
	Date	Maximum Ozone (ppm)	Time (EDT)	Date	Maximum Ozone (ppm)	Time (EDT)	Date	Maximum Ozone (ppm)	Time (EDT)
1	8/9	.118	1800	8/2	.053	1800	8/3	.049	1200
	8/19	-	-	8/12	.112	1000	8/21	-	-
	8/23	-	-	8/15	.056	1100 - 1200	8/25	.035	1400
	8/24	-	-	9/20	.119	1700	9/4	.045	1100 - 1300
	9/6	.086	1200 - 1400	9/27	.079	1400	9/25	.050	1500
2	8/9	.105	1800	8/2	-	-	8/3	-	-
	8/19	.104	1700	8/12	.083	1300	8/21	.042	1600
	8/23	.080	1500 - 1600	8/15	.049	1200 - 1400	8/25	.019	0300
	8/24	.121	1400 - 1600	9/20	.099	1300 - 1400	9/4	.048	1000 - 1100
	9/6	.129	1900	9/27	.075	1600	9/25	.053	1500
3	8/9	.119	2200	8/2	.095	1700	8/3	.059	1600
	8/19	.142	2100	8/12	.099	1600	8/21	.072	1700
	8/23	.108	1700	8/15	.099	1300	8/25	.058	0100
	8/24	.133	1500	9/20	.075	1600	9/4	.049	0100
	9/6	.131	2000	9/27	.096	1600	9/25	.056	1500
4	8/9	.090	1400	8/2	.111	1500	8/3	.062	1300
	8/19	.123	1300	8/12	.112	1500	8/21	.054	1500
	8/23	.101	1600	8/15	.133	1400	8/25	.048	0200
	8/24	.126	1500 - 1600	9/20	.074	1600	9/4	.063	0900
	9/6	.145	1600	9/27	.094	1700	9/25	.060	1400

Table 14. (Continued)

Site	Photochemically Active Days with Strong Transport			Photochemically Active Days with No Well-Defined Transport			Days with Little Photochemical Activity		
	Date	Maximum Ozone (ppm)	Time (EDT)	Date	Maximum Ozone (ppm)	Time (EDT)	Date	Maximum Ozone (ppm)	Time (EDT)
5	8/9	-	-	8/2	-	-	8/3	-	-
	8/19	.105	1700	8/12	-	-	8/21	.075	1700
	8/23	.111	1800	8/15	.133	1400 - 1500	8/25	-	-
	8/24	.127	1600	9/20	.113	1700	9/4	-	-
	9/6	-	-	9/27	.100	1200, 1800	9/25	.076	1000
South Broad Street	8/9	.060	1400, 2000	8/2	.030	1500	8/3	.020	1200 - 1300
	8/19	.100	1400, 1800	8/12	.060	1400	8/21	.050	1600
	8/23	.080	1700	8/15	.040	1200, 1300	8/25	.020	0300 - 0500
	8/24	.100	1600	9/20	.180	1700	9/4	.030	1000 - 1800
	9/6	.070	1600	9/27	.040	1400	9/25	.030	1300 - 1600

4.6 CASE STUDIES OF OZONE AND PRECURSOR TRANSPORT

This section presents analyses of two cases of strong ozone transport into the Philadelphia area which illustrate transport situations of particular importance.

Synoptic scale trajectories referred to in the following discussion were drawn using the assumption of geostrophic flow (motion parallel to isobars). Pressure data was obtained from three hourly National Weather Service surface maps. The geostrophic assumption necessarily means that trajectories are calculated for parcels above the friction layer (above approximately 500 meters AGL). A more complete discussion of trajectories can be found in Saucier (1955) and Pettersen (1956).

Mesoscale trajectories were derived using surface wind information from five locations within the study area. The interpolation scheme uses weighted averages of the wind components. The weighting factors are inversely proportional to the square of the distance between the air parcel and the wind site. More weight is given to wind observations when they are made directly upwind or downwind of the air parcel than when they are removed to one side. This feature is included to reflect the tendency of winds to change more rapidly in cross-streamline directions than along the streamlines.

4.6.1 August 22, 23, 24

This series of days represents the only extended "transport episode" observed during the monitoring period for which data are available. It illustrates the cumulative effect of a somewhat prolonged transport situation.

High pressure centered over the study area on August 22 moved to the south and was centered over North Carolina by August 24. A frontal passage on August 25 terminated the episode. Figure 29 shows the surface synoptic weather situation on August 23. The location of the high over the Washington, D.C. area was also observed on several other strong transport days.

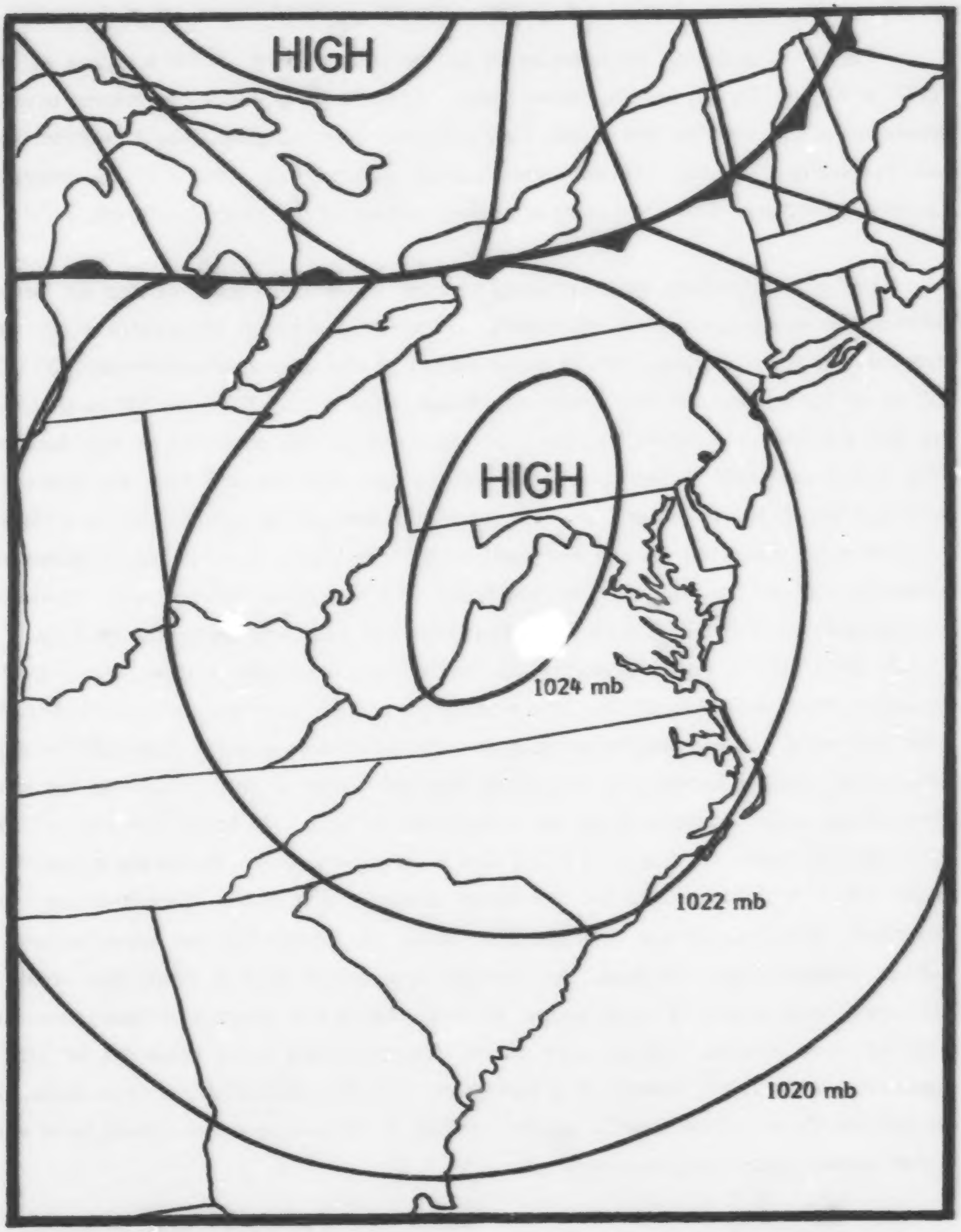
HIGH
HIGH
1024 mb
1022 mb
1020 mb

FIGURE 29. Synoptic situation, 0700 EDT, August 23, 1979.

Figure 30 presents trajectories of air parcels arriving in Philadelphia at 1400 EDT on August 22, 23, and 24, respectively. As the high pressure cell moved over the study area and then to the south, flow changed from variable, mostly northerly, to southwesterly. The last two days show parcels approaching along a broad, anticyclonically curved arc. This trajectory is typical of most of the cases examined.

Using five surface wind stations, surface trajectories for selected air parcels within the study area were developed. Figures 31 through 33 present study area trajectories for three parcels: (1) an air parcel at the upwind boundary at 0700 EDT; (2) an air parcel located near downtown Philadelphia at 0700 EDT; and (3) an air parcel at Site 5 at the time when the maximum ozone level was observed at that location. The mesoscale trajectories for August 22 indicate that surface flow was somewhat weaker than on August 23 and 24. Air parcels located at the upwind boundary (Site 3) at 0700 were advected toward the east, across the primary source areas (downtown Philadelphia) and to the east or southeast. Air parcels located over downtown Philadelphia at 0700 EDT were advected from the west and southwest on August 23 and 24 but from the north on August 22. In fact, a southwesterly flow regime did not establish itself until August 23. These same air parcels were then advected eastward over downwind areas generally arriving at locations 40 km or more downwind by early afternoon. Unfortunately, no monitoring was performed in that portion of the study area. High ozone concentrations were recorded at Site 5 on these three days (0.11, 0.11, and 0.13 ppm on August 22, 23, and 24, respectively). Backward trajectories from Site 5 were developed for the hours during which these concentrations were observed. The trajectories indicate that these air parcels did not traverse metropolitan Philadelphia. Instead, the parcels approached Site 5 from the west to northwest over primarily rural areas, although the urban centers of Bethlehem and Reading were upwind. Since high ozone concentrations were observed at Site 5 apparently without the benefit of a trajectory over the Philadelphia source areas, the air parcels shown which have a trajectory over these source areas should have even higher ozone concentrations downwind.

Vertical profiles obtained upwind over Site 2 by the instrumented helicopter during the early morning hours are presented in Figures 34 through 36. Average ozone concentrations aloft increase slightly from day to day. Late morning flights actually

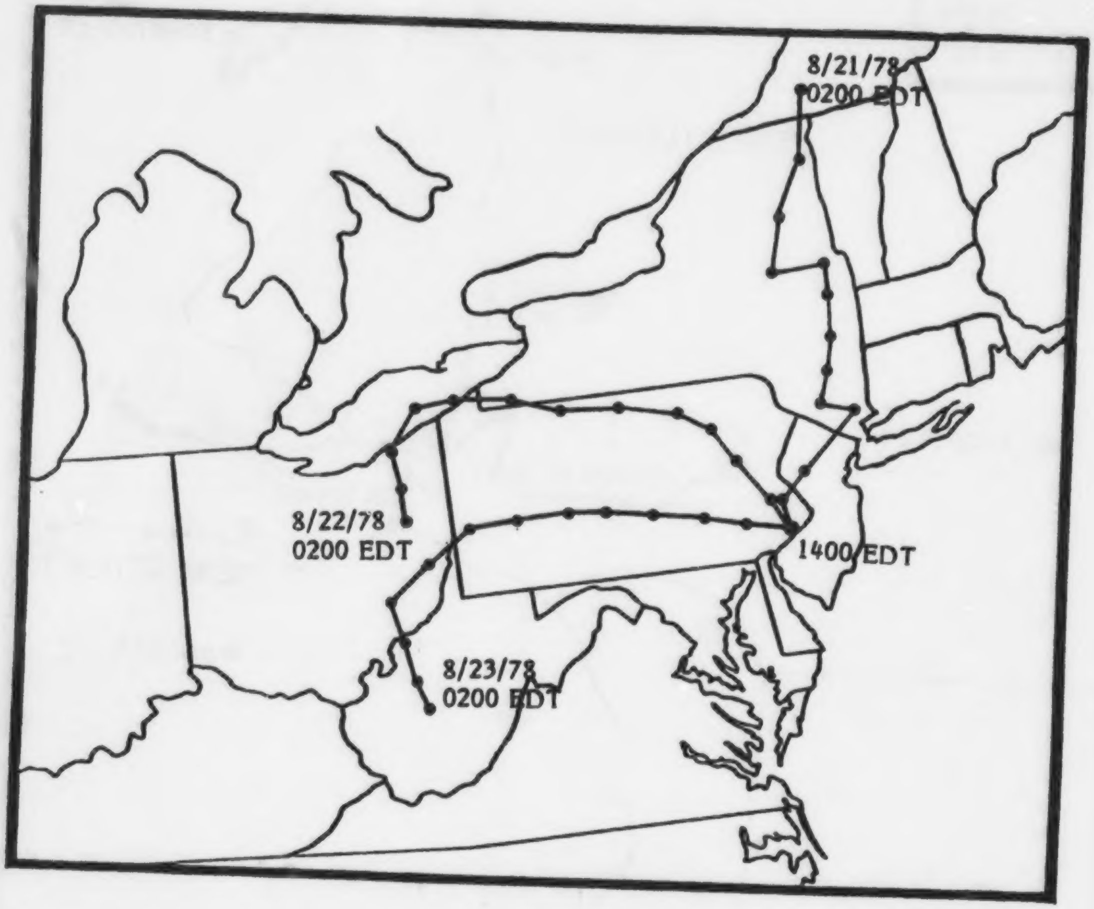
8/21/78
0200 EDT
8/22/78
0200 EDT
1400 EDT
8/23/78
0200 EDT

FIGURE 30. Estimated 36-hour air parcel trajectories beginning 0200 EDT on August 21, 22, and 23 and ending 1400 EDT on August 22, 23, and 24, respectively. (•) indicates position every 3 hours.

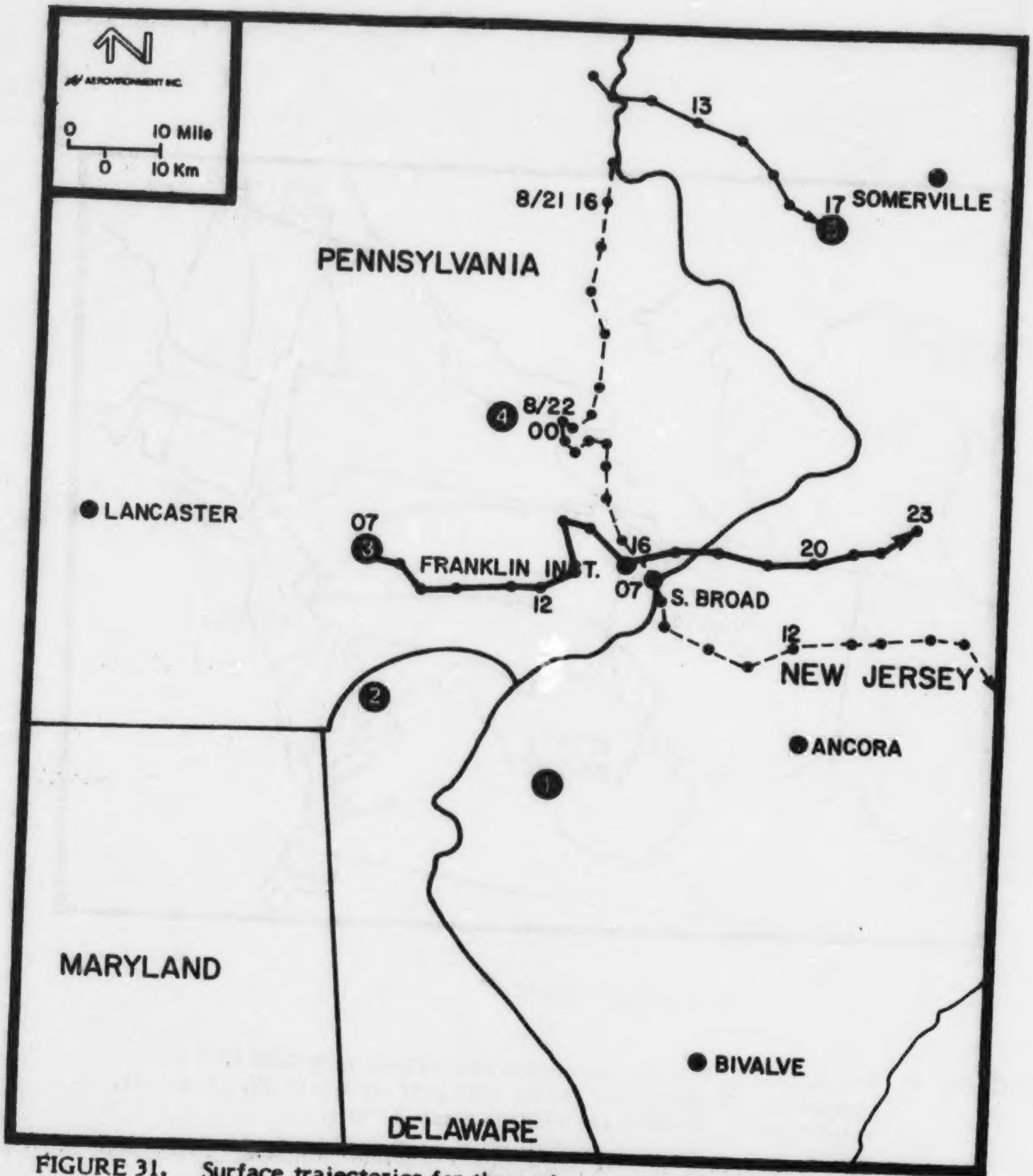
N
AEROVIRONMENT INC.
0
10 Mile
0
10 Km
13
8/21 16
17
SOMERVILLE
5
PENNSYLVANIA
4
8/22
00
LANCASTER
07
3
FRANKLIN INST.
12
16
20
23
07
S. BROAD
12
NEW JERSEY
2
ANCORA
1
MARYLAND
BIVALVE
DELAWARE

FIGURE 31. Surface trajectories for three air parcels located within the study area on August 22, 1978. Numbers shown indicate clock hour in EDT. Times and locations of the air parcels tracked are as follows:

——— : 0700 at Site 3 (Upwind Boundary)
- - - : 0700 at South Broad Street (Downtown)
——— : 1700 at Site 5 (High Ozone Level)

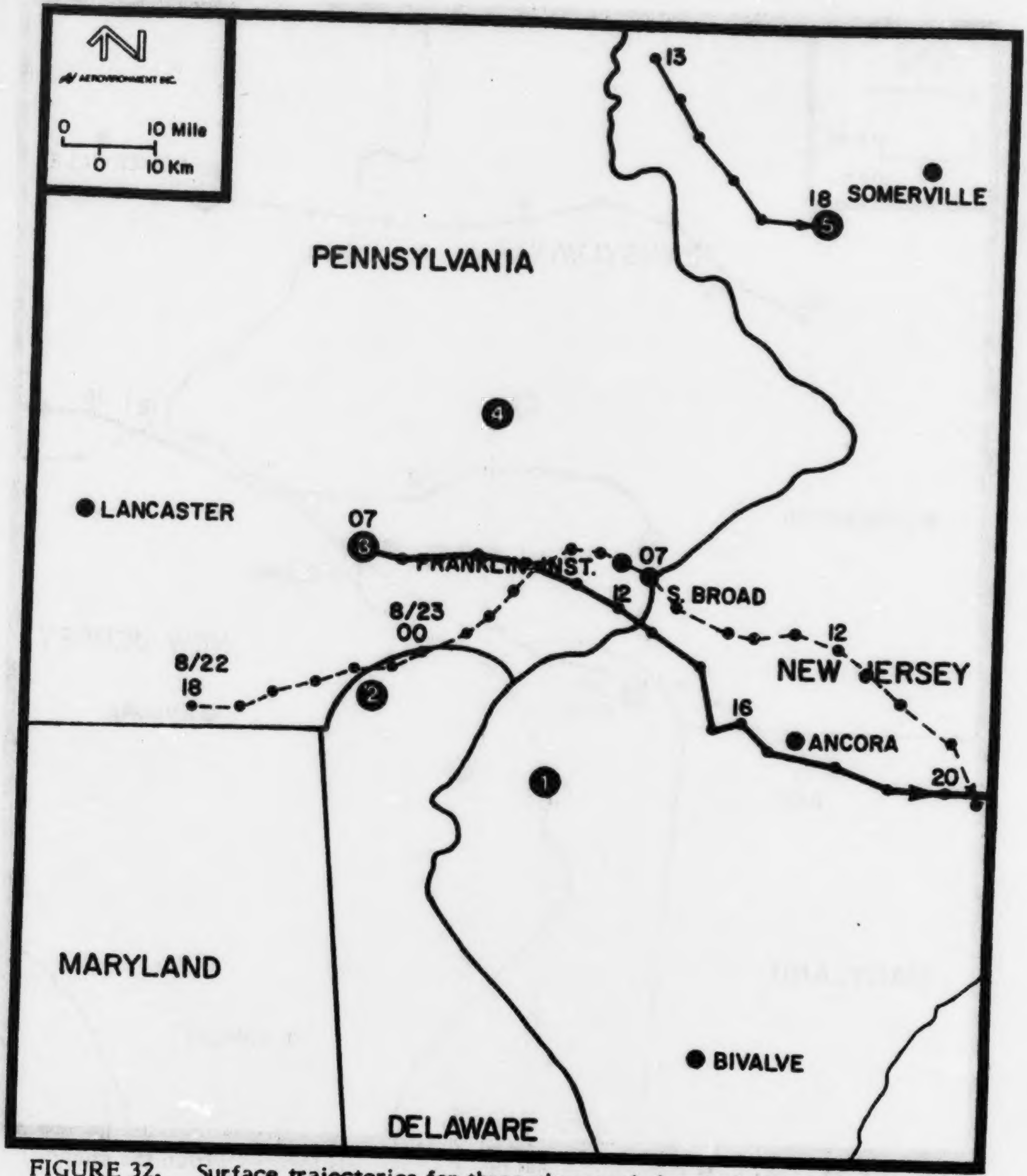
N
AEROVIRONMENT INC.
0
10 Mile
0
10 Km
PENNSYLVANIA
NEW JERSEY
MARYLAND
DELAWARE
SOMERVILLE
LANCASTER
FRANKLIN INST.
S. BROAD
ANCORA
BIVALVE
13
18
07
07
12
12
8/23
00
8/22
18
16
20
1
2
3
4
5

FIGURE 32. Surface trajectories for three air parcels located within the study area on August 23, 1978. Numbers shown indicate clock hour in EDT. Times and locations of the air parcels tracked are as follows:

—: 0700 at Site 3 (Upwind Boundary)
- - -: 0700 at South Broad Street (Downtown)
—: 1700 at Site 5 (High Ozone Level)

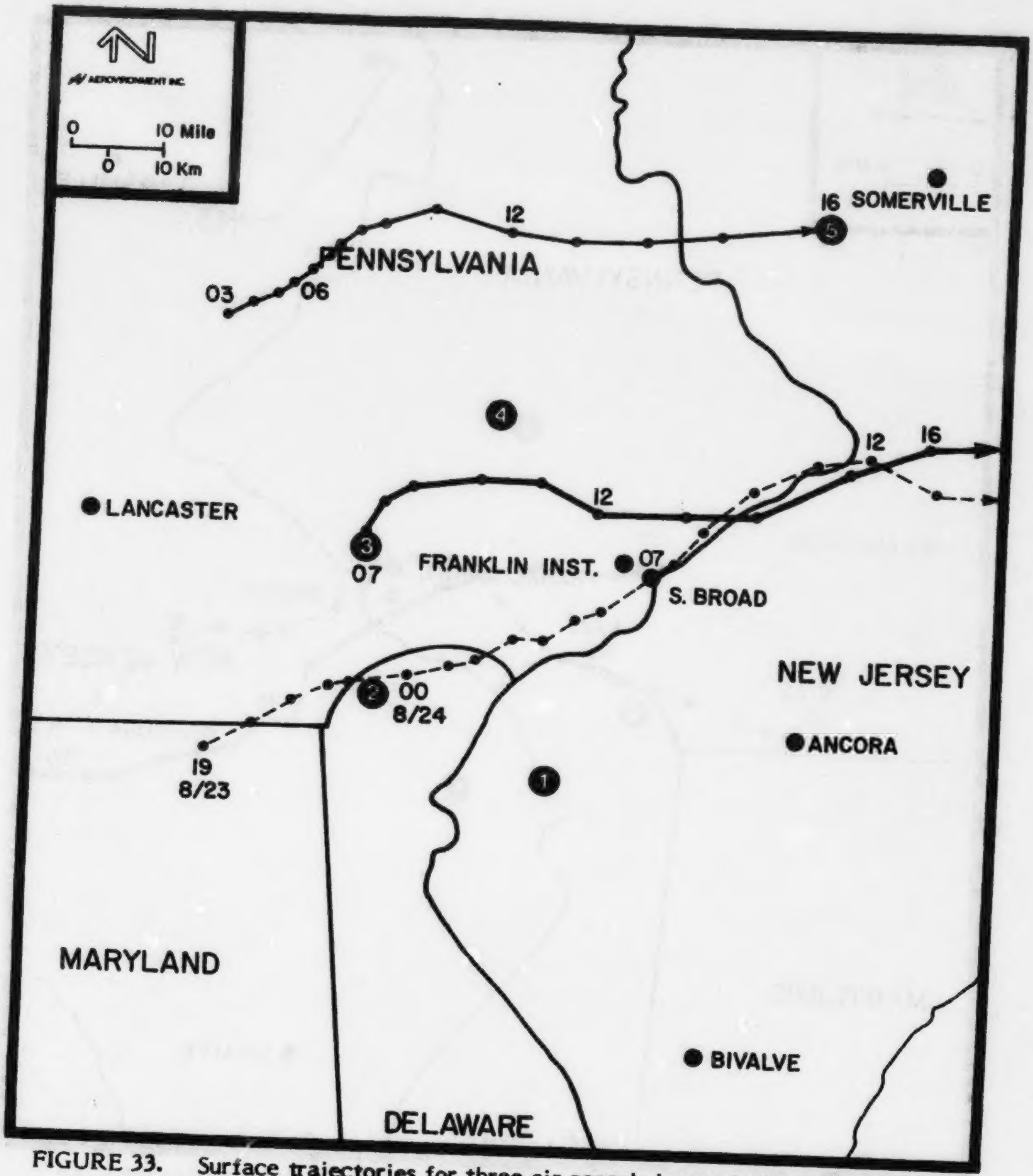
N
AEROVIRONMENT INC.
0
10 Mile
0
10 Km
PENNSYLVANIA
03
06
12
16
SOMERVILLE
5
4
LANCASTER
3
07
12
FRANKLIN INST.
07
S. BROAD
12
16
NEW JERSEY
2
00
8/24
19
8/23
ANCORA
1
MARYLAND
BIVALVE
DELAWARE

FIGURE 33. Surface trajectories for three air parcels located within the study area on August 24, 1978. Numbers shown indicate clock hour in EDT. Times and locations of the air parcels tracked are as follows:

——: 0700 at Site 3 (Upwind Boundary)
- - -: 0700 at South Broad Street (Downtown)
——: 1700 at Site 5 (High Ozone Level)

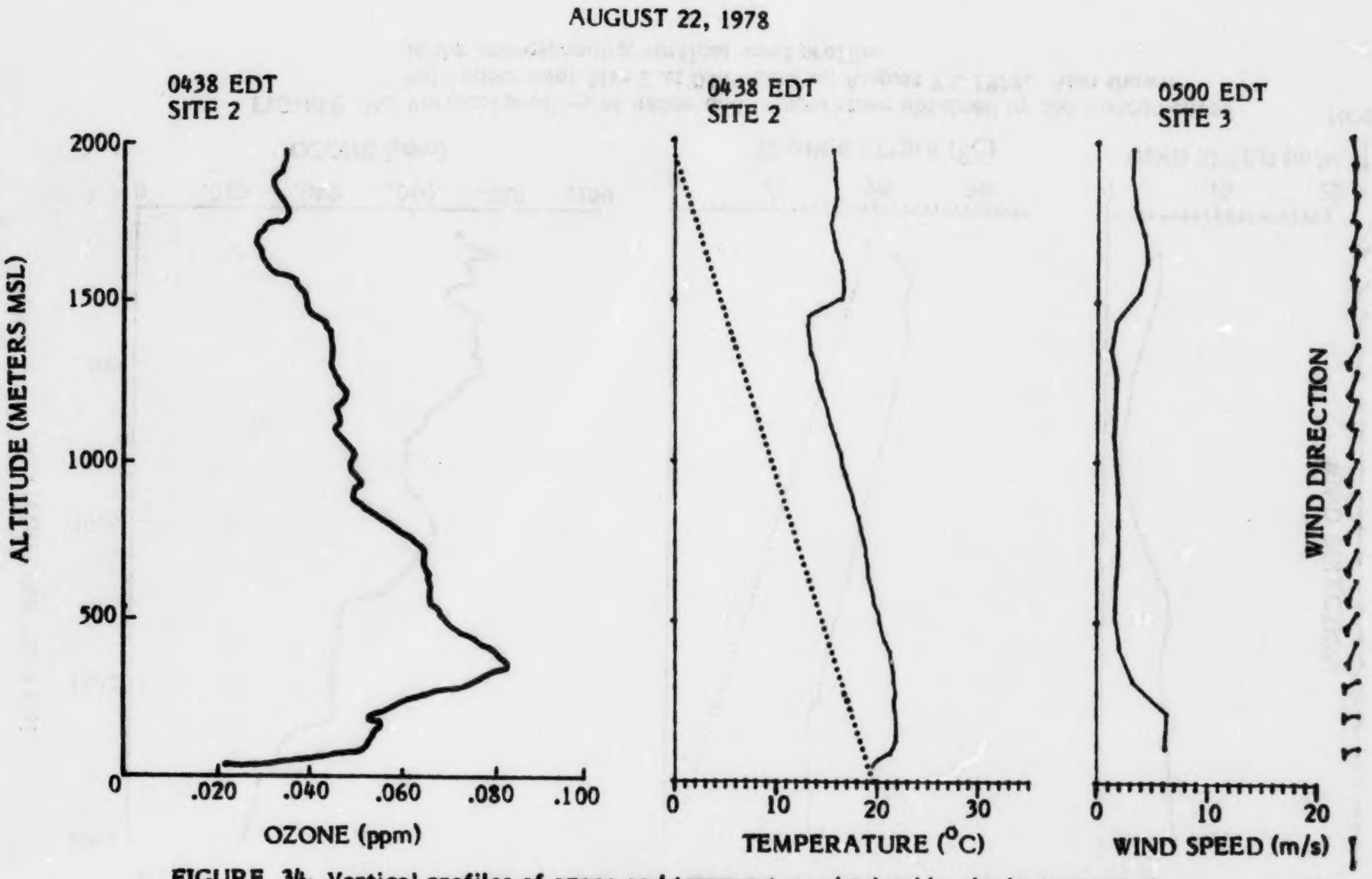

FIGURE 34. Vertical profiles of ozone and temperature obtained by the instrumented helicopter over Site 2 at 0438 EDT on August 22, 1978. Also shown is the corresponding vertical wind profile.

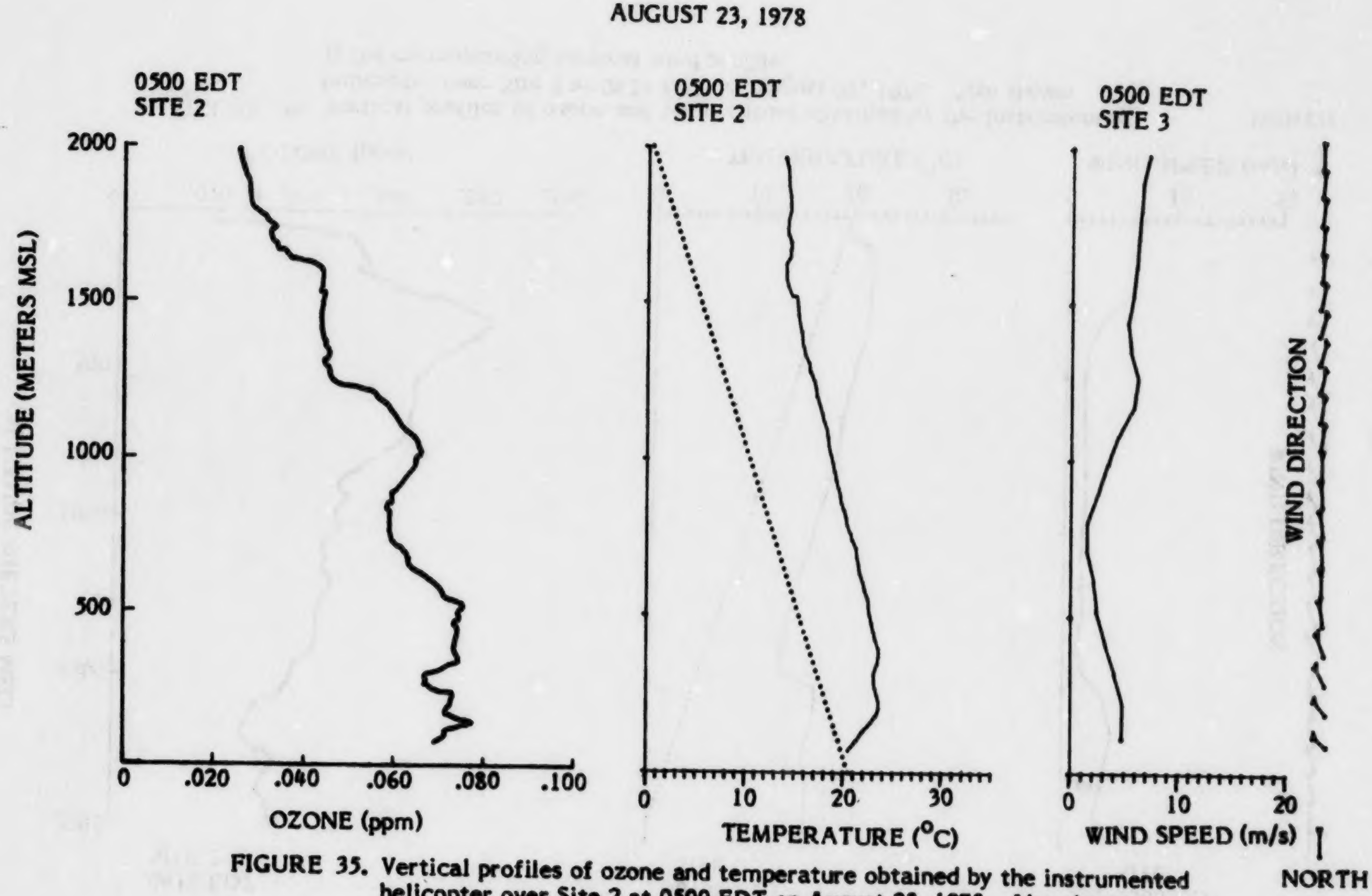

FIGURE 35. Vertical profiles of ozone and temperature obtained by the instrumented helicopter over Site 2 at 0500 EDT on August 23, 1978. Also shown is the corresponding vertical wind profile.

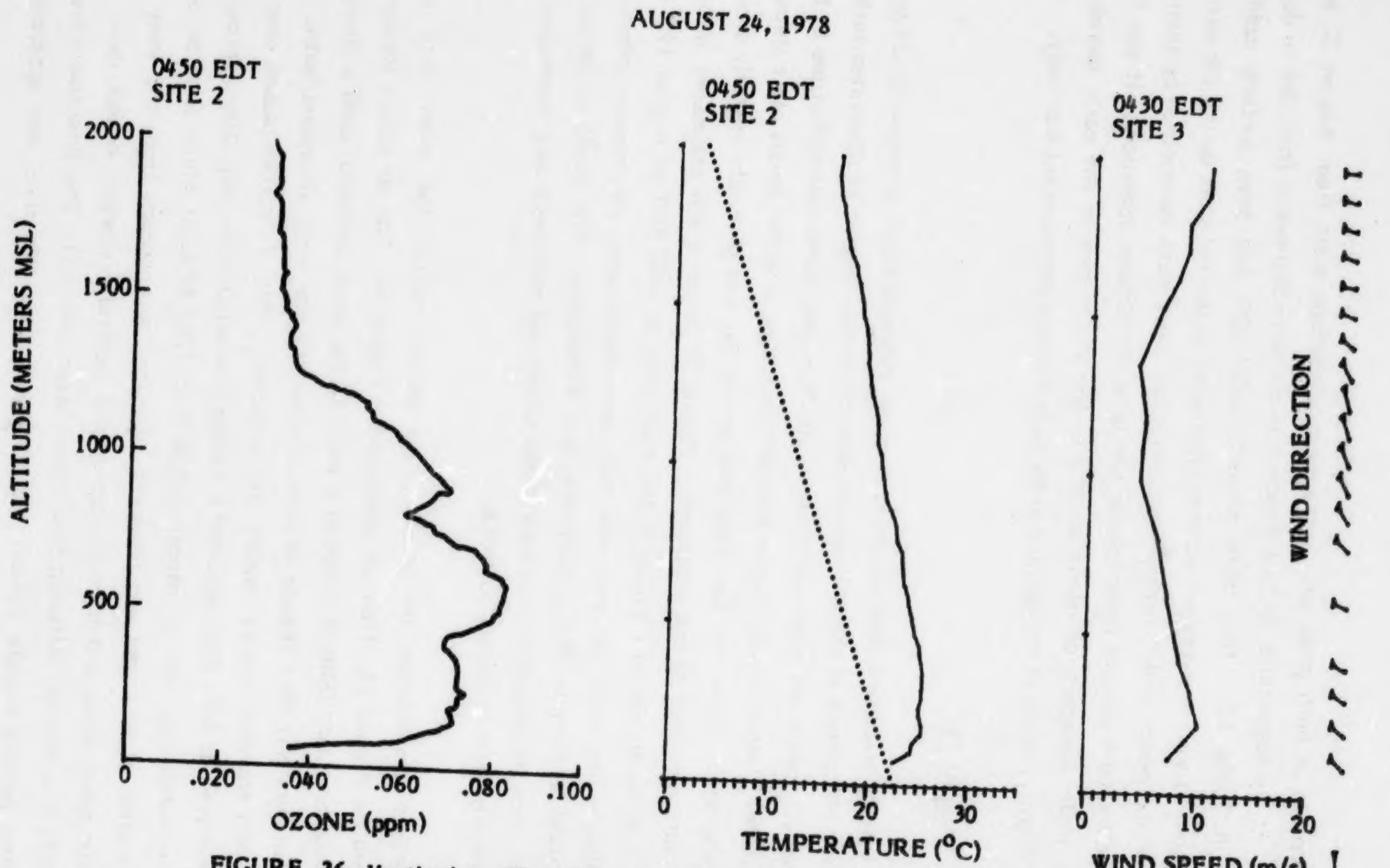

FIGURE 36. Vertical profiles of ozone and temperature obtained by the instrumented helicopter over Site 2 at 0450 EDT on August 24, 1978. Also shown is the corresponding vertical wind profile.

show a decrease in both peak and average concentrations aloft from August 22 to August 24. At the same time, surface concentrations were increasing from day to day as shown in Table 15. This table presents 1100 EDT and peak surface ozone concentrations as well as average concentrations aloft at upwind sites during the early morning for the period under study. Concentrations aloft were determined by taking the average in the transport layer (above the layer of surface depletion). It can be seen that while transport of ozone aloft into the study area in the early morning increases slightly, ozone at the surface in the late morning increases substantially.

4.6.2 August 19

On several transport days, oxides of nitrogen concentrations in excess of .05 ppm in the lower 300 meters of the atmosphere were observed. August 19 illustrates such a case. The NO_x peaks are often associated with depressed ozone concentrations at the same altitude. August 19 also shows dramatic increases in ozone levels aloft through the morning hours. Flow over the study area on this day was generally westerly around high pressure centered to the southwest. Figure 37 presents the estimated 36-hour trajectory of an air parcel arriving in the study area at 1400 EDT on August 19. The parcel approached from the west and may have passed over the heavily urbanized areas around Washington D.C., Baltimore, and Wilmington. The speed of the parcel was slow, thus its residence time over these cities was relatively long increasing its ozone and precursor transport potential.

Surface trajectories for selected air parcels within the study area were developed for August 19. They are presented in Figure 38. The air parcel located at the upwind boundary (Site 2) followed a track to the south-southeast until a stronger, more southwesterly flow regime became dominant in the early afternoon hours. The parcel then traveled rapidly toward the northeast. The air parcel passed over the downtown area at 0700 EDT followed a similar downwind trajectory after approaching from the northwest. An air parcel at Site 5 at 1700 EDT, at which time an ozone concentration of 0.11 ppm was observed, appeared to approach from the west over primarily rural areas although Allentown was generally upwind on this day. This trajectory is somewhat different than others after 1200 EDT. The flow that advected the other parcels rapidly toward the northeast after this time was apparently a

Table 15. OZONE CONCENTRATIONS (in ppm) AT UPWIND STATIONS ON AUGUST 22, 23, AND 24.

Site	Surface						Aloft		
	1100 EDT			Maximum			Average of Transport Layer[a]		
	8/22	8/23	8/24	8/22	8/23	8/24	8/22	8/23	8/24
1	-	-	-	-	-	-	.070	.070	.072
2	.058	.063	.076	.079	.080	.121	.062	.068	.070
3	.069	.075	.103	.108	.108	.133	.052	-	-
4	.056	.074	.093	.098	.101	.126	-	-	.055

[a] Obtained by instrumented helicopter at approximately 0500 EDT.

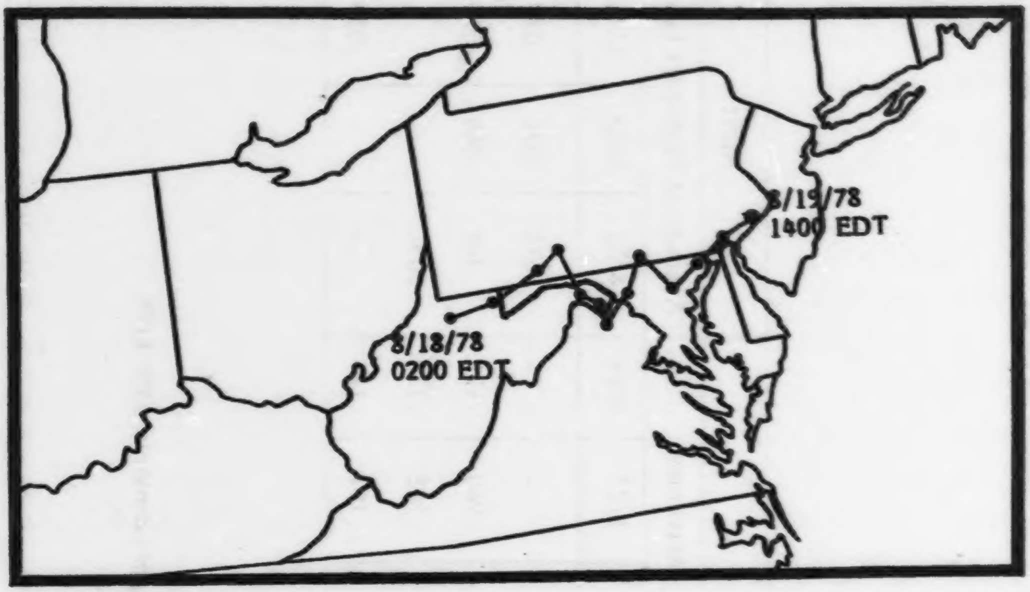
8/19/78
1400 EDT
8/18/78
0200 EDT

FIGURE 37. Air parcel trajectory beginning 0200 EDT August 18 and ending 1400 EDT on August 19. (•) indicates position every three hours.

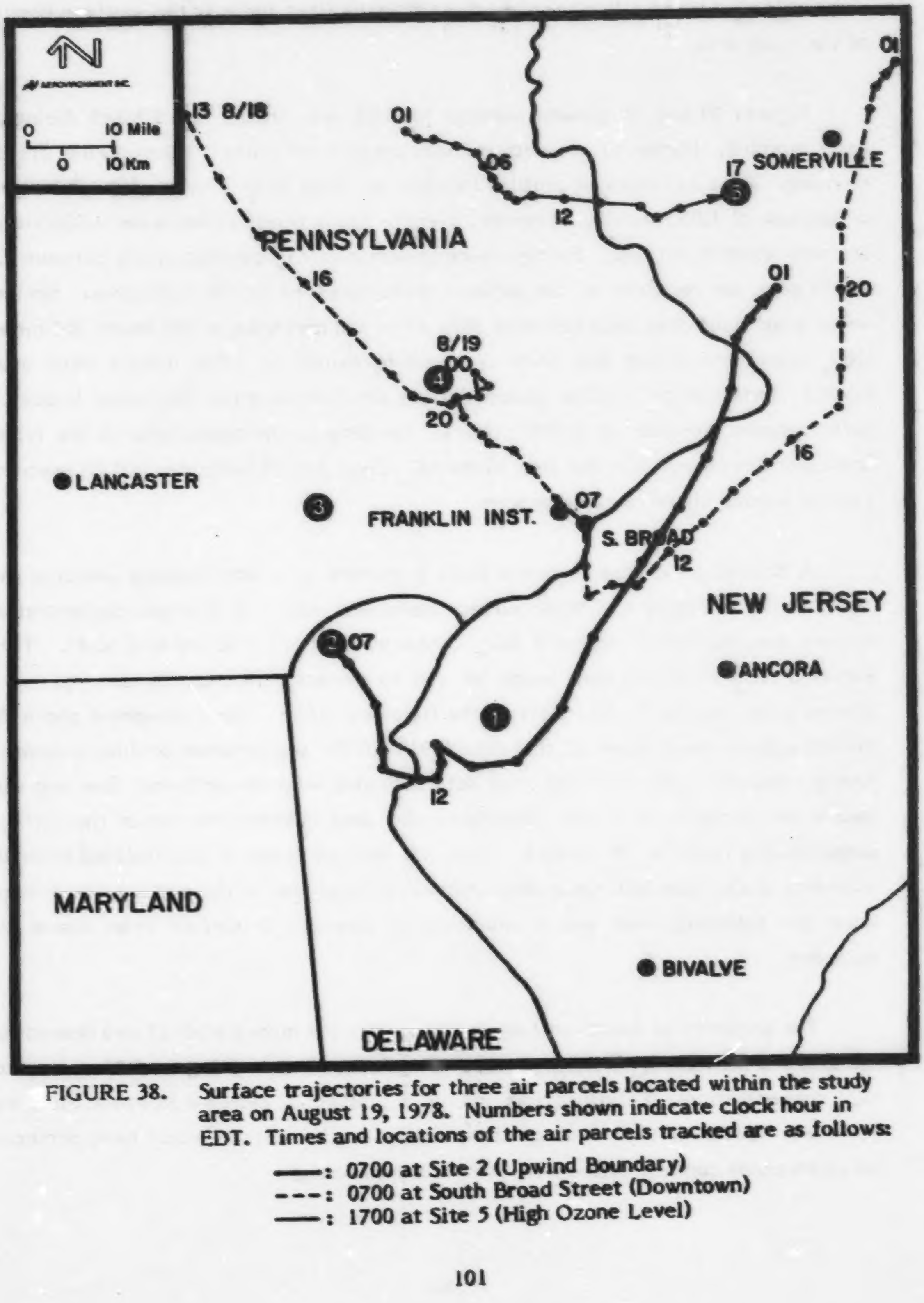
N
AEROVIRONMENT INC.
0
10 Mile
0
10 Km
13 8/18
01
06
12
17
SOMERVILLE
5
01
PENNSYLVANIA
16
01
20
8/19
00
4
20
16
LANCASTER
3
FRANKLIN INST.
07
S. BROAD
12
NEW JERSEY
2
07
ANCORA
1
12
MARYLAND
BIVALVE
DELAWARE

FIGURE 38. Surface trajectories for three air parcels located within the study area on August 19, 1978. Numbers shown indicate clock hour in EDT. Times and locations of the air parcels tracked are as follows:

——: 0700 at Site 2 (Upwind Boundary)
- - -: 0700 at South Broad Street (Downtown)
——: 1700 at Site 5 (High Ozone Level)

mesoscale phenomenon (e.g., modified sea breeze) affecting only the southern portions of the study area.

Figures 39 and 40 present vertical profiles over Sites 1 and 2 taken during the early morning. Figure 41 presents vertical profiles over Site 1 taken during the late morning. The early morning profiles indicate an ozone peak in excess of 0.060 ppm at an altitude of 1,000 meters. However, average ozone levels in the lower 1,000 meters are only about 0.040 ppm. Perhaps more important, NO_x concentrations between 0.01 to .05 ppm, not recorded at the surface, were observed by the helicopter. Simultaneous pibal wind data indicate weak flow from the northeast in the lower 500 meters (NO_x layer) and strong flow from the west-northwest at 1,000 meters (high ozone layer). Temperature profiles obtained from the instrumented helicopter indicate a surface-based inversion up to 250 meters. The flow in the ozone layer is the typical transport direction, while the flow in the NO_x layer puts Philadelphia and its precursor sources upwind of the monitoring sites.

A dramatic increase in ozone aloft is evident in a late morning sounding over Site 1 shown in Figure 41. While surface ozone and oxides of nitrogen concentrations remain low, somewhat elevated NO_x concentrations are still evident aloft. These elevated NO_x concentrations might be due to impacts from an elevated plume or plumes from sources located west of the Delaware River. The atmosphere above 200 meters appears well mixed at this time (0919 EDT): temperature profiles indicate a nearly adiabatic lapse rate and pibal data indicates west-to-northwest flow and wind speeds are in excess of 5 m/s. Acoustic radar data indicate the top of the surface-based mixing layer is 130 meters. Thus, the surface layer is still isolated from the transport aloft. Acoustic radar data indicate a rapid rise in the surface-based mixed layer the following hour and a simultaneous increase in surface level ozone was recorded.

The sequence of events on August 19 suggests the mixing aloft of two distinct air masses, one containing substantial ozone levels and one containing somewhat elevated NO_x concentrations. Following this mixing, a substantial increase in ozone aloft was recorded. Later in the morning, after mixing to the surface would have occurred, elevated ozone concentrations were seen at the surface.

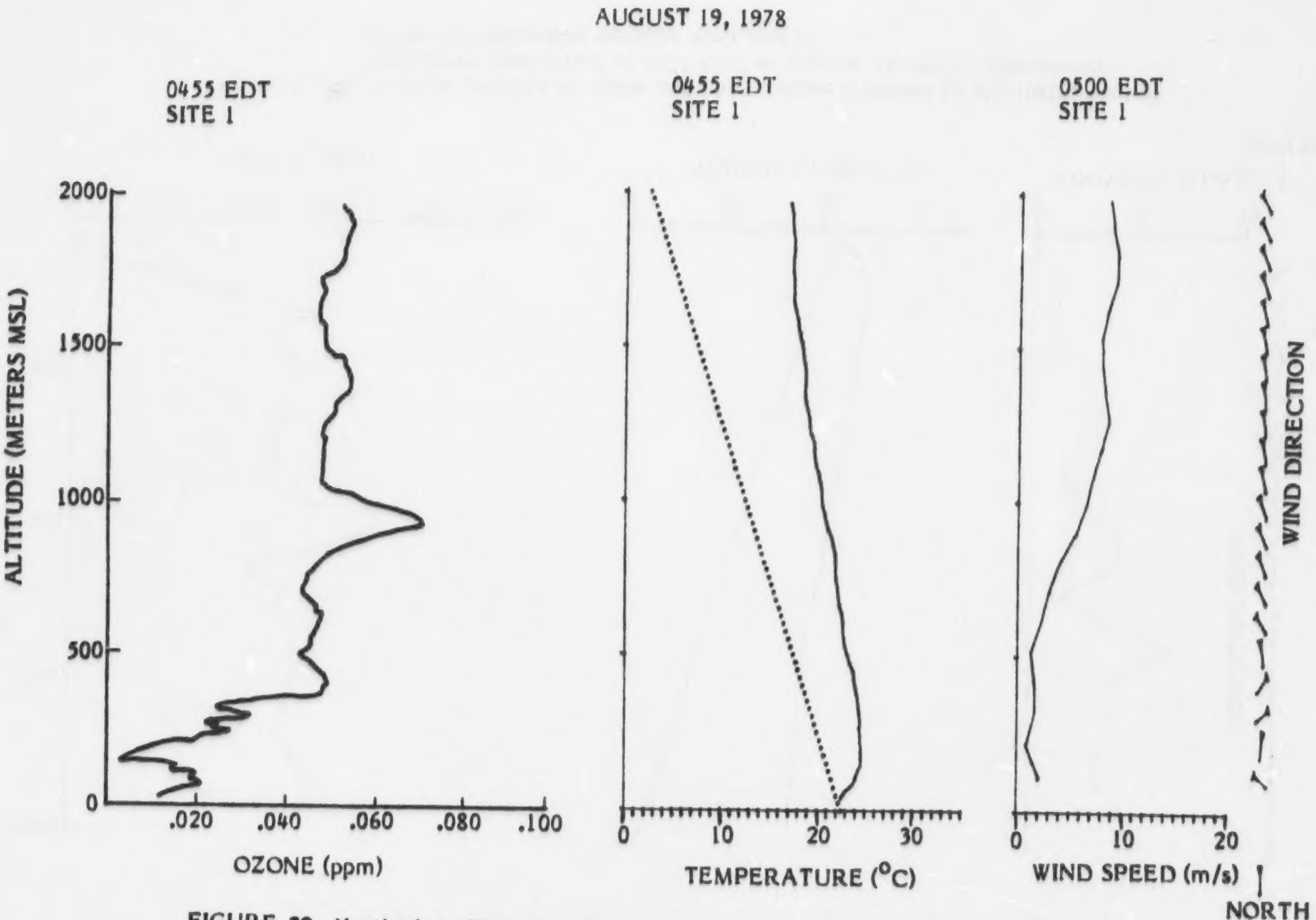

FIGURE 39. Vertical profiles of ozone and temperature obtained by the instrumented helicopter over Site 1 at 0455 EDT on August 19, 1978. Also shown is the corresponding vertical wind profile.

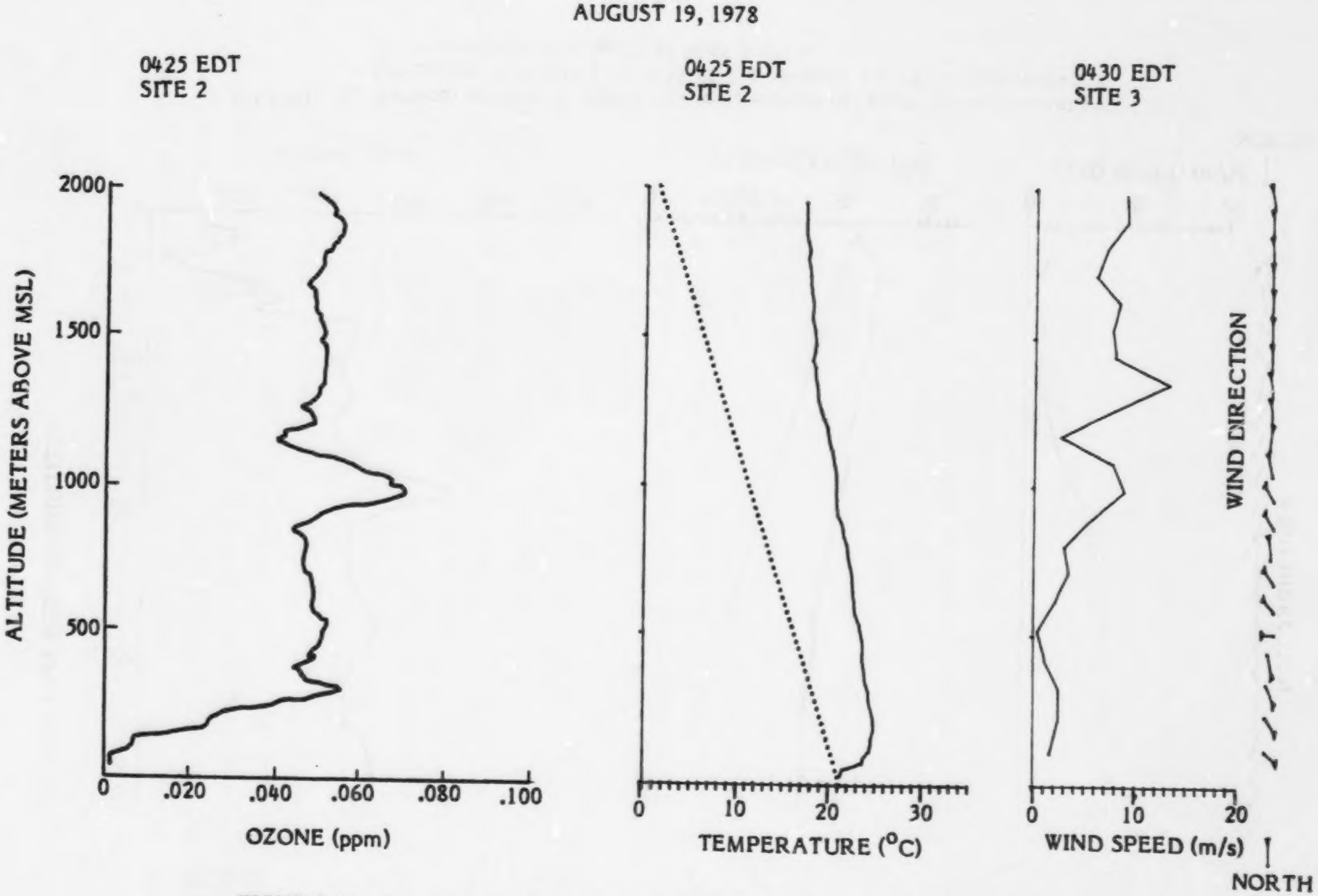

FIGURE 40. Vertical profiles of ozone and temperature obtained by the instrumented helicopter over Site 2 at 0425 EDT on August 19, 1978. Also shown is the corresponding vertical wind profile.

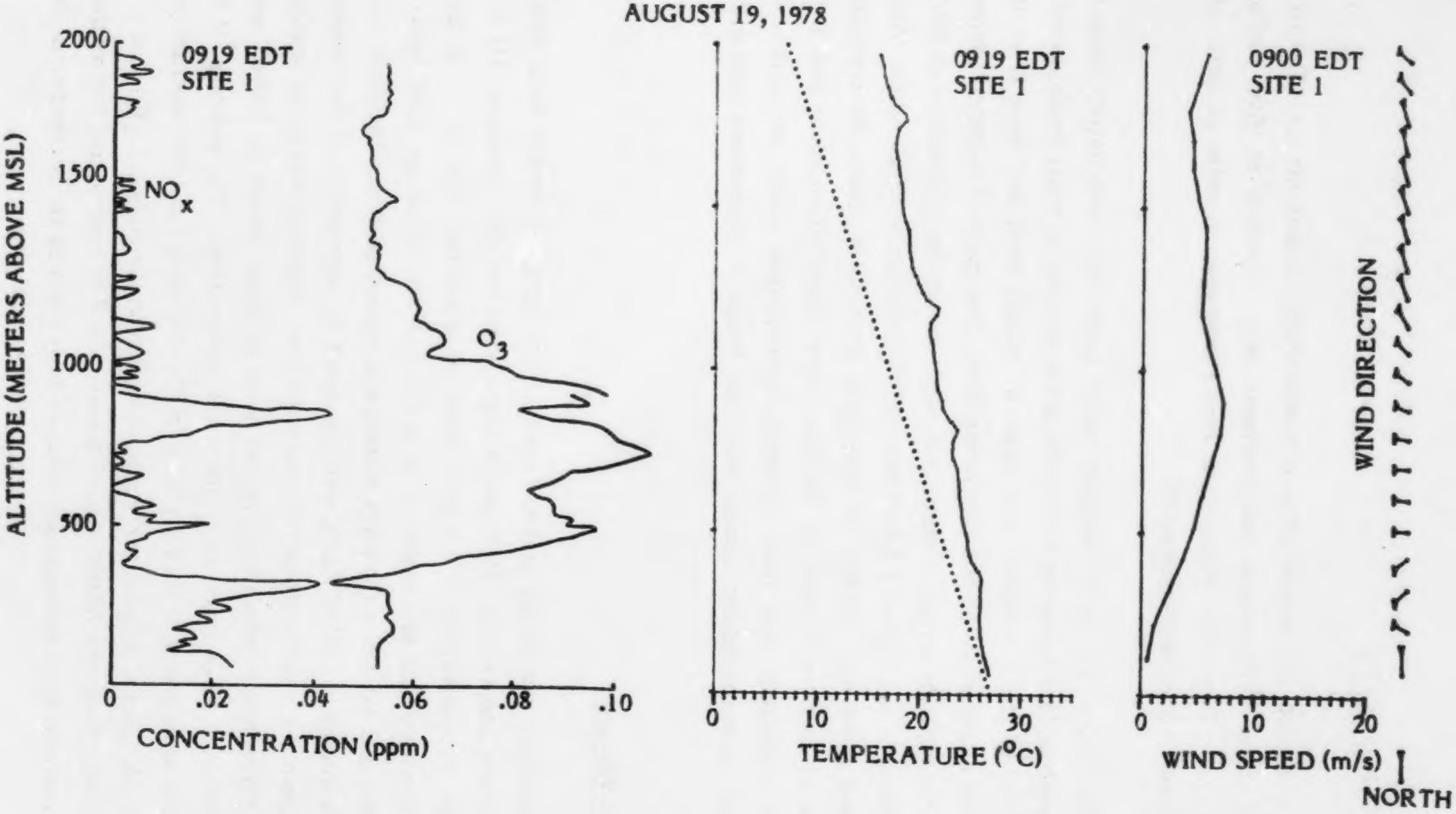

FIGURE 41. Vertical profiles of ozone, oxides of nitrogen, and temperature obtained by the instrumented helicopter over Site 1 at 0919 EDT on August 19, 1978. Also shown is the corresponding vertical wind profile.

4.7 HYDROCARBON DATA

The study produced two sets of data on hydrocarbons in ambient air. The first set consisted of total hydrocarbon and methane data collected at five surface monitoring stations. These are reported as hourly averages in units of parts per million carbon (ppm C) (methane equivalent).

In addition, about 135 grab samples were taken into evacuated sampling containers and analyzed for a sequence of hydrocarbon species by Scott Environmental Technology. Some of these samples were taken at ground level and some from the aircraft at various altitudes above the monitoring sites. Two pairs of matched samples taken mid-way through the program were split, with one set being analyzed at EPA's Environmental Science and Research Laboratory (EPA-ESRL) in North Carolina. Aside from this one test there was virtually no replication of samples. Since the unreacted composition was of primary interest all samples were taken before noon; thus little photoreaction is expected. For many samples, hydrocarbons which are within the capability of the chromatographic system were not found in measurable concentrations.

4.7.1 Data Validity

The hydrocarbon monitoring systems used in this program sensed total hydrocarbon and methane separately. Methane is segregated for four reasons: (1) It is present in large concentrations (~1.4 ppm) even in unpolluted air; (2) it is quite unreactive in photochemical processes; (3) it is emitted into urban air from leaks in natural gas lines; and (4) the air quality standard is stated on a non-methane basis. Non-methane hydrocarbon (NMHC) data were obtained by subtraction of the methane concentration from the total hydrocarbon concentration. Although this is the standard procedure for hydrocarbon monitoring it can lead to large errors in NMHC when methane constitutes a large fraction of the total hydrocarbon. For example, if the total hydrocarbon were found to be 2.3 ± 0.1 ppm C (~5% error) and the methane was found to be 2.0 ± 0.1 ppm C (~5% error) the subtraction would yield 0.3 ± 0.1 ppm C of NMHC (30% error). Thus, the NMHC concentration found by subtracting the methane measurement from the total hydrocarbon measurement has a larger percent error than the two measurements have separately. There is added uncertainty because the two concentrations are measured from separate, not necessarily identical, air samples.

Another problem arises from the units used in the various measurements. Since the average molecular weights of the mixture of hydrocarbons which make up the total is not known it is necessary to report NMHC as parts per million carbon (ppm C), relying on the fact that the flame detector responds approximately according to the concentration of organically bound carbon in the sample. The speciation analyses were (except for the samples analyzed by the EPA) all reported as parts per million compound (that is, by moles). To make a comparison of the hydrocarbon breakdown with the NMHC derived from the continuous monitoring instrument it was necessary to multiply the concentration of each hydrocarbon by its carbon number to obtain ppm C, then to sum all species concentrations. To the extent that many hydrocarbons present in too small concentrations to be quantified might collectively make a significant contribution to the NMHC, this sum would fall short of that reported by the continuous monitor.

The two samples analyzed by EPA-ESRL and Scott are presented below for comparative purposes. One pair was time-integrated and one-hour samples and one pair was helicopter grab samples. The Scott samples were converted to ppm carbon to compare directly with the EPA-ESRL samples. Also shown is the NMHC concentration reported by the continuous surface monitor for comparison with the integrated samples. The values were:

Concentration (ppm C)					
			NMHC		
Date	Hour (EDT)	Site	EPA Analysis	Scott Analysis	Surface Monitor
Aug. 24, 1978	0500-0600	3	1.58	0.55	0.1
Aug. 24, 1978	0611*	4	1.59	1.65	—

*helicopter grab samples.

The comparisons are not very encouraging and the reason for the discrepancy is not known. Although the total NMHC reported by EPA and Scott correspond well for the 0611 grab sample, concentrations of individual compounds do not. The EPA and Scott samples all showed substantial amounts of two oxygenates (acetaldehyde and acetone) although the agreement on concentration was not close. These oxygenates may be artifacts. If so, they must be introduced by the sampling system rather than the analytical instrument since they appear in both EPA and Scott analyses. These two oxygenates together accounted for about 0.3 ppm to 0.4 ppm of the 1.58 to 1.59 total shown above so their elimination would not remove the discrepancy with the hourly average concentration obtained by continuous monitoring.

The Scott gas chromatographic analyses offered only one pair of duplicate analyses. One of these samples was taken in a glass container and, like so many of the other samples, showed a high (30 ppb) concentration of acetaldehyde. It also showed anomalous concentrations of propane and isobutane and, to a lesser extent, n-butane. Contamination with some kind of liquefied petroleum gas is suspected. The agreement of this glass container sample with the matching metal sampler was not good.

In view of the inconsistency among surface samples it was not possible to discern a trend or gradient in comparing aircraft samples with simultaneous ground samples. Both showed the frequent presence of acetaldehyde and acetone.

From the data it is unclear which system is reporting the more nearly correct concentrations. Even though the absolute magnitude of NMHC or individual species of hydrocarbon is unknown, relative values can nevertheless be used to indicate the location and the nature of hydrocarbon sources. This is demonstrated in the following section.

4.7.2 Analysis of Continuous Hydrocarbon Monitoring

The flux of hydrocarbon past the air monitoring station can be used so evaluate source strength. Flux of NMHC can be estimated by multiplying wind speed by concentration. A source strength which is constant should yield a constant flux in spite of variations in wind speed (for comparable vertical mixing). Thus, multiplication by wind speed corrects for the greater dilution of hydrocarbon caused by higher wind speed. Tables 16 through 20 present joint frequency distributions of wind direction and NMHC flux for the five monitoring sites. Some wind directions are associated with frequent occurrences of high flux values, which suggests that important NMHC sources lie in those directions. For example, Site 1 showed high fluxes from the north-northwest to east-northeast. Site 5 showed high flux values associated with flows from the north-northeast to east-northeast and south-southwest to west-northwest wind directions. Site 5 was above Washington's Crossing where north-northeast to east-northeast flow of pollutants from north New Jersey or New York could emanate and south-southwest to west-southwest would come from Philadelphia.

It is important to note that the wind directions of maximum NMHC flux differ from the wind directions associated with high ozone readings (see Figures 13 through 17). For example, the quadrant associated with high ozone concentrations at Sites 1, 2, and 3 is southwest while the quadrants associated with maximum NMHC flux at these same sites are northeast for Site 1, east for Site 2 (secondary maximum from the south), and southeast for Site 3. These maximum NMHC wind directions put Philadelphia and the industrialized corridor to the southwest along the Delaware River upwind of Sites 1, 2, and 3. In contrast, the ozone roses seem to rule out Philadelphia as a major area of origin. The data thus indicates that high NMHC concentrations at monitoring sites around Philadelphia are due to short-range transport from the urban core and are not related to long-range transport.

4.7.3 Hydrocarbon Species Analysis

Neither of the two analytical systems used in this program was especially designed to detect organic compounds emitted by vegetation, even though isoprene and the monoterpines (e.g., alpha and beta pinene) are within the C_2-C_{10} carbon range specified. With very few exceptions the compounds which were detected are all hydrocarbons typical of gasoline and/or auto exhaust; that is, they range from C_2 to about C_{10} and include all the major structural types. The only exceptions are acetaldehyde and acetone which were present in many samples, often at high concentration, even when the concentrations of other compounds were low or

Table 16. NON-METHANE HYDROCARBON (NMHC) FLUX ROSE FOR SITE 1.

Wind Direction	NMHC Flux ($\mu g/m^2/sec$)					
	0-300	301-600	601-900	900-1200	1200-1500	>1500
N	20	9	2	2	0	0
NNE	31	9	8	0	1	1
NE	23	11	5	3	0	0
ENE	22	15	1	2	0	0
E	17	2	1	0	0	0
ESE	24	3	0	0	0	0
SE	24	0	0	0	0	0
SSE	25	0	0	0	0	0
S	44	2	0	0	0	0
SSW	52	6	1	0	0	0
SW	47	2	0	0	0	0
WSW	24	1	0	0	0	0
W	11	1	0	0	0	0
WNW	2	1	0	0	0	0
NW	7	1	0	0	0	0
NNW	8	2	3	0	0	1

Table 17. NON-METHANE HYDROCARBON (NMHC) FLUX ROSE FOR SITE 2.

Wind Direction	NMHC Flux (μg/m^2/sec)					
	0-300	301-600	601-900	900-1200	1200-1500	>1500
N	31	16	7	0	0	0
NNE	24	15	6	1	1	1
NE	27	21	4	2	0	0
ENE	25	17	9	4	2	1
E	18	17	5	5	0	2
ESE	13	13	8	1	0	2
SE	13	5	3	2	0	0
SSE	4	11	7	1	2	2
S	26	14	10	2	1	5
SSW	14	17	3	4	1	1
SW	24	9	5	0	0	0
WSW	34	23	8	4	0	0
W	32	20	5	0	0	0
WNW	30	9	1	1	0	0
NW	24	22	8	2	0	0
NNW	8	2	3	0	0	1

Table 18. NON-METHANE HYDROCARBON (NMHC) FLUX ROSE FOR SITE 3.

Wind Direction	NMHC Flux ($\mu g/m^2/sec$)					
	0-300	301-600	601-900	900-1200	1200-1500	>1500
N	65	6	3	2	0	0
NNE	46	9	2	1	0	0
NE	30	5	0	0	0	0
ENE	23	6	4	0	1	0
E	27	5	0	0	1	0
ESE	24	3	3	0	1	0
SE	18	5	5	8	5	3
SSE	29	14	7	2	2	0
S	65	9	4	3	1	0
SSW	129	12	4	4	0	1
SW	93	7	1	2	2	0
WSW	69	1	0	0	0	0
W	56	5	0	0	1	0
WNW	39	1	1	0	0	1
NW	46	5	1	1	0	0
NNW	49	1	3	2	1	0

Table 19. NON-METHANE HYDROCARBON (NMHC) FLUX ROSE FOR SITE 4.

Wind Direction	NMHC Flux (µg/m^2/sec)					
	0-300	301-600	601-900	900-1200	1200-1500	>1500
N	20	2	0	0	0	0
NNE	20	2	0	1	0	0
NE	40	4	0	0	0	0
ENE	37	5	2	0	0	0
E	21	1	1	0	0	0
ESE	19	5	0	0	0	0
SE	31	2	0	0	0	0
SSE	55	12	4	1	0	0
S	101	22	3	1	1	2
SSW	126	14	3	4	2	0
SW	58	5	0	0	0	0
WSW	37	1	0	0	0	0
W	39	0	0	0	0	0
WNW	31	2	0	0	0	0
NW	67	1	0	0	0	0
NNW	46	0	1	0	0	0

Table 20. NON-METHANE HYDROCARBON (NMHC) FLUX ROSE FOR SITE 5.

Wind Direction	NMHC Flux (μg/m^2/sec)					
	0-300	301-600	601-900	900-1200	1200-1500	>1500
N	61	0	1	0	0	0
NNE	50	1	2	1	1	1
NE	93	12	4	3	1	0
ENE	79	14	5	3	0	4
E	27	5	3	0	0	0
ESE	11	1	0	0	0	0
SE	13	2	0	0	0	1
SSE	34	0	2	1	0	0
S	27	1	0	0	0	0
SSW	53	17	3	4	1	0
SW	112	16	11	5	5	0
WSW	96	13	6	4	3	2
W	66	8	2	4	0	3
WNW	39	5	2	2	0	0
NW	44	1	1	0	0	1
NNW	81	1	2	0	1	0

immeasurable. There are no clearly recognized major sources of these two compounds although acetone has uses as a solvent, and it and acetaldehyde would be expected in small amounts in exhaust gas or as a product of atmospheric reactions. There is a likelihood that both are artifacts of the sampling system. A few samples showed extreme values (several ppm) of ethene with no other anomalies. Most of these excess ethene samples were from Site 1 but some were aircraft samples. Another anomaly was found in two samples, excessive amounts of propane and isobutane. These two samples had nothing apparent in common. Liquified petroleum gas would be the most probable source of propane but it would usually be accompanied by n-butane.

One sample in particular, aside from the acetone and acetaldehyde found, looked much like auto exhaust in composition, although quite dilute. It shows paraffins and aromatics in about the expected propositions, as well as acetylene (10 ppb) and propene (4.3 ppb) at about the ratio recognized for auto exhaust. However, only a trace of ethene was found. One sample showed 0.7 ppb of 1.3 butadiene, a common industrial emission. It is moderately ractive in the atmosphere but not more so than some detectable olefins.

Three unsaturated hydrocarbons, acetylene, ethene and propene, provide both a unique marker for auto exhaust and an index of degree of reaction. Only two samples reported values for both acetylene and ethene and only three samples reported both propene and acetylene. One sample showed a propene/acetylene ratio of 4.9/78 (ppb/ppb) and an ethene/acetylene ratio of 41/78. Another sample contained more propene than acetylene but only trace amounts of ethene. In unreacted auto exhaust the ratio of propene to acetylene should be (based on old data) about 0.20 to 0.25 (by moles). In one sample the ratio was 0.43 and again ethene was listed as trace. With such a very limited data base, and one so inconsistent, conclusions on the nature of the sources cannot be very firm.

5. PERFORMANCE EVALUATION OF SELECTED MEASUREMENT TECHNIQUES

Ozone and precursors transported into an urban area affect the maximum ozone concentrations observed downwind of the urban area during the afternoon. Thus, in developing control strategies for attaining and/or maintaining the ozone standard, state agencies should take into consideration the impact of transported ozone and precursors. The first step in determining this impact is to determine the quantity of ozone and precursors transported into the urban area.

Ozone and precursors could be transported over long distances overnight either within or above the surface layer. However, near-surface transport of ozone and nitrogen oxides over any appreciable period during the night appears to be limited by surface sinks. The effects of the surface layer on hydrocarbon removal rates is, on the other hand, less well understood. Limited data (U.S. EPA, 1977) indicate that concentrations of hydrocarbons are significantly reduced in the urban plume as it travels away from an urban area, but it is not known what mechanisms are contributing to the reduction or to what extent. This data showed that hydrocarbon concentrations upwind of urban areas are usually in the 0.1 - 0.3 ppmC range; the data obtained at the rural surface stations in Philadelphia during the summer of 1978 also fall within this range.

In contrast, because scavengers and sinks are lacking, high concentrations of ozone and, possibly, precursors can remain in and above stable layers aloft and be transported over long distances overnight. Vertical pollutant concentration profiles taken in Philadelphia show that, in the early morning hours, high levels of ozone are found above the surface-based inversion. As the inversion is eroded away, ozone is mixed down to the surface. Surface measurements in rural areas near Philadelphia on photochemically active days show an increase in ozone concentrations of about .02 ppm immediately following the breakup of the surface based inversion. Little or no change in hydrocarbons and oxides of nitrogen concentrations at the surface monitoring stations is observed following the inversion breakup. Soundings also reveal that the oxides of nitrogen concentrations in layers aloft are usually about the same as those at the surface, typically in the range of 0.01 to 0.05 ppm.

Calculations using EKMA (U.S. EPA, 1978) suggest that the observed levels of transported hydrocarbons and oxides of nitrogen would not appreciably increase the maximum ozone concentration downwind of an urban area. However, the observed levels of ozone transported aloft and mixed to the surface could appreciably alter the maximum ozone concentration.

The discussion above implies that the technique used for measuring the transport of ozone must be able to quantify the level of ozone that is transported aloft overnight, since this seems to be the primary parameter (in terms of pollutants) that would cause a significant increase in the maximum ozone concentration in an urban area. It also implies that if there is a need to quantify the precursors entering an urban area, measurements of precursors made at a properly located upwind surface monitoring station should suffice.

The rest of this chapter evaluates the capability of the five measurement techniques tested in Philadelphia. The evaluation emphasizes the ability of the technique to quantify the ozone transported aloft.

5.1 SURFACE MONITORING NETWORK

Since ozone trapped aloft overnight is mixed downward to the surface after the breakup of the surface based inversion, it seems possible that surface measurements could be used to quantify the ozone transported aloft. It has been suggested that surface measurements between 1100 and 1300 LDT would be most indicative of ozone levels aloft (U.S. EPA, 1977). The data collected during the summer of 1978 allowed this hypothesis to be tested.

As pointed out in the preceding chapter, eight days during the 1978 summer study were identified to be significant transport days. On five of those eight days, soundings of pollutant concentrations were made with the U.S. EPA helicopter. Data collected during the first flight of each day, prior to the onset of significant solar radiation, should show the amount of ozone transported aloft overnight.

In the preceding chapter, it was also pointed out that during those days, Sites 1, 2 and 3 were upwind sites. On four of those five days, Site 4 was also upwind of Philadelphia. Early morning soundings, however, were taken mostly over Sites 1, 2, and 3, with only one sounding taken over Site 4 on the transport days.

A comparison of the ozone concentrations aloft with average ozone readings between 1100 - 1300 EDT at surface stations shows that the average surface ozone readings are almost always higher than the ozone concentrations aloft. The average of the differences between surface concentrations between 1100 - 1300 EDT and the concentrations aloft is 0.014 ppm. Therefore, using the average surface reading between 1100 - 1300 EDT would possibly overestimate the amount of ozone transport aloft.

If we knew when ozone transported aloft is mixed to the surface we would have an idea of when surface readings would be representative of ozone concentrations transported aloft. During this study, therefore, an acoustic radar was installed at Site 1. Records from the radar indicate when the surface inversion begins to be eroded and when mixing in the vertical is no longer inhibited. Figure 42 is a record taken on the morning of August 23, 1978. It shows stable atmospheric structure extending from the surface to 220 m between 0700 - 1000 EDT. From then until 1100 EDT the surface mixed layer deepens, after which mixing in the vertical is uninhibited.

The acoustic radar provided information on the time when vertical mixing became uninhibited on four of the five selected days on which transport was determined to be significant and helicopter data were available. On August 19 and 22, mixing to the surface of pollutants trapped aloft was thus determined to begin at 1000 EDT, while on August 23 and 24 the mixing began at 1100 EDT.

Surface ozone readings at Sites 1 through 4 were compared against the peak ozone reading aloft. Ozone data for three time periods were used for the comparison: (1) the average for the hour following the mixing, (2) the average reading between 1100 - 1300 EDT, and (3) the average reading between 1000 - 1200 EDT. Table 21 presents the comparison. The limited data available for the comparison indicate that the average reading for the hour following the mixing and the average reading between

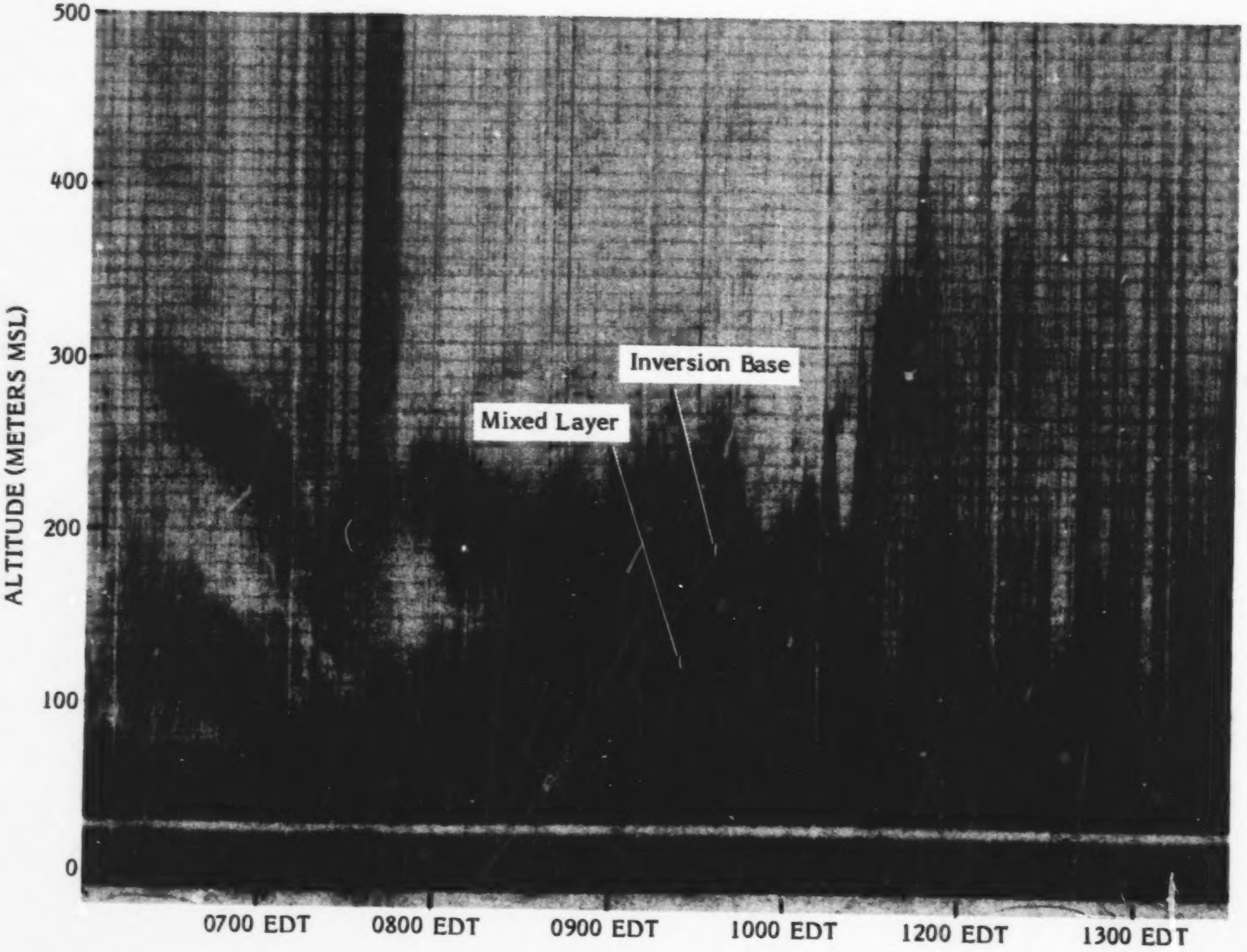

FIGURE 1. Acoustic radar record at Site 1 on August 23, 1978.

Table 21. COMPARISON OF SURFACE OZONE CONCENTRATION WITH EARLY MORNING CONCENTRATION ALOFT. ALL CONCENTRATIONS ARE IN ppm.

Site	Date[a]	Peak O_3 Concentration Aloft[b]	Time When Mixing is Completed (EDT)[c]	Averaged Ozone Concentration Above the Surface Stable Layer[b]	Hourly Reading After Mixing is Completed	Average Reading Between 1100-1300 EDT	Average Reading Between 1000-1200 EDT
1	8/9	.083	-	.082	-	.108	.095
	8/19	.065	1000	.047	.071	-	.087
	8/22	.085	1000	.070	-	-	-
	8/23	.080	1100	.070	-	-	-
	8/24	.080	1100	.072	-	-	-
2	8/9	.085	-	.081	-	.072	.069
	8/19	.066	1000	.048	.047	.070	.059
	8/22	.078	1000	.062	.053	.058	.056
	8/23	.072	1100	.068	.063	.061	.059
	8/24	.077	1100	.070	.076	.083	.066
3	8/9	.083	-	.081	-	.089	.075
	8/19	.084	1000	.071	.066	.103	.084
	8/22	.068	1000	.052	.058	.071	.064
4	8/24	.070	1100	.068	.093	.106	.081

Note: [a] Dates on which early morning soundings were performed.

[b] From early morning helicopter soundings.

[c] Times determined from acoustic radar data at Site 1. Time when mixing is completed is assumed to be the same at other sites.

1000 - 1200 EDT are both more representative of the ozone level aloft than is the average reading between 1100 - 1300 EDT. The average difference between the reading immediately following the mixing and the peak ozone aloft is .005 ppm. The two largest differences occur on August 24 at Site 4 and on August 19 at Site 1. Using the 1100 - 1300 EDT averages for these two instances would result in an even larger difference, hence would be a poorer indicator of ozone levels aloft.

This analysis indicates that surface monitoring stations located upwind of urban areas can be used to measure ozone transported aloft. Hourly averaged readings taken during the hour immediately following the completion of the mixing between the surface layer and the layers aloft are representative of the ozone levels aloft. The time when mixing is completed is best determined by an acoustic radar, which gives a continuous record of the atmospheric structure. If the radar is not available, the average over the two hours during which the mixing is completed (1000 - 1200 EDT in Philadelphia) would also be a good indicator of ozone levels aloft.

Given that upwind surface monitoring stations can be used to quantify the ozone transported aloft, the next question is how many upwind stations are necessary. In other words, is there a significant horizontal gradient upwind in the ozone concentrations aloft?

On the transport days when helicopter soundings are available, ozone concentrations aloft over all the upwind sites are almost identical (within .01 ppm of one another). Table 21 shows that the only major gradient in ozone concentrations was observed on August 19, when the average ozone aloft above Site 3 was .071 ppm while the ozone concentration above Site 1 was .047 ppm and above Site 2 was 0.048 ppm. Another day when there is a definite difference is August 22, when helicopter data shows that the concentration aloft increased from .052 ppm over Site 3, to .062 ppm over Site 2, to .070 ppm over Site 1. At the surface stations, however, Site 2 had a reading of .053 and Site 3 a reading of .058. No surface data were recorded at Site 1 at that time. The helicopter soundings indicate that, in general, the ozone-laden plume aloft traveling into Philadelphia is fairly homogeneous, and there being little variation on most days in ozone concentrations aloft along the upwind boundary of the urban area.

Table 21 also shows that data at a surface station used to represent ozone aloft compares well with that at another surface station. The largest difference was on August 19 when Site 1 was higher than Site 2 by .024 ppm.

Therefore, the data indicate that, for Philadelphia, one monitoring station upwind of the urban core is sufficient to acquire measurements closely indicative of the ozone being transported aloft. However, one upwind site might not suffice for measuring ozone transported into other East Coast and Midwest cities. Consideration should be given to the probability of significant and varying ozone concentrations from other nearby, upwind urban sources. But, for most isolated Central and Western cities, one monitoring station would probably be satisfactory.

5.2 AIRBORNE MEASUREMENTS BY DEDICATED INSTRUMENTED AIRCRAFT

The capability of a dedicated instrumented aircraft to measure the ozone transported aloft is obvious if the equipment is properly calibrated and the operators are well trained. The soundings taken by the U.S. EPA helicopter provided valuable information on the vertical ozone profiles. From surface measurements, one can only infer the ozone levels aloft. Using a dedicated instrumented aircraft, one can directly measure the ozone concentration aloft. As discussed earlier, it is probably not necessary to measure precursor levels aloft. Precursor levels can best be measured at the surface. Thus, the combination of a dedicated instrumented aircraft measuring ozone and lapse rate and an upwind surface monitoring station measuring ozone, precursors, and wind would provide all the needed information on the transport of ozone and precursors into an urban area.

5.3 AIRBORNE MEASUREMENTS BY A PORTABLE INSTRUMENT PACKAGE

The portable instrument package is another direct means of measuring the concentration of ozone aloft. The reliability of the data obtained was tested by comparing the data with that collected by the U.S. EPA helicopter. Eight side-by-side flights were made with the portable instrument package and the helicopter in Philadelphia. Figure 43 presents a comparison of soundings made with both methods. The helicopter data is faithfully duplicated by the profile obtained with the portable

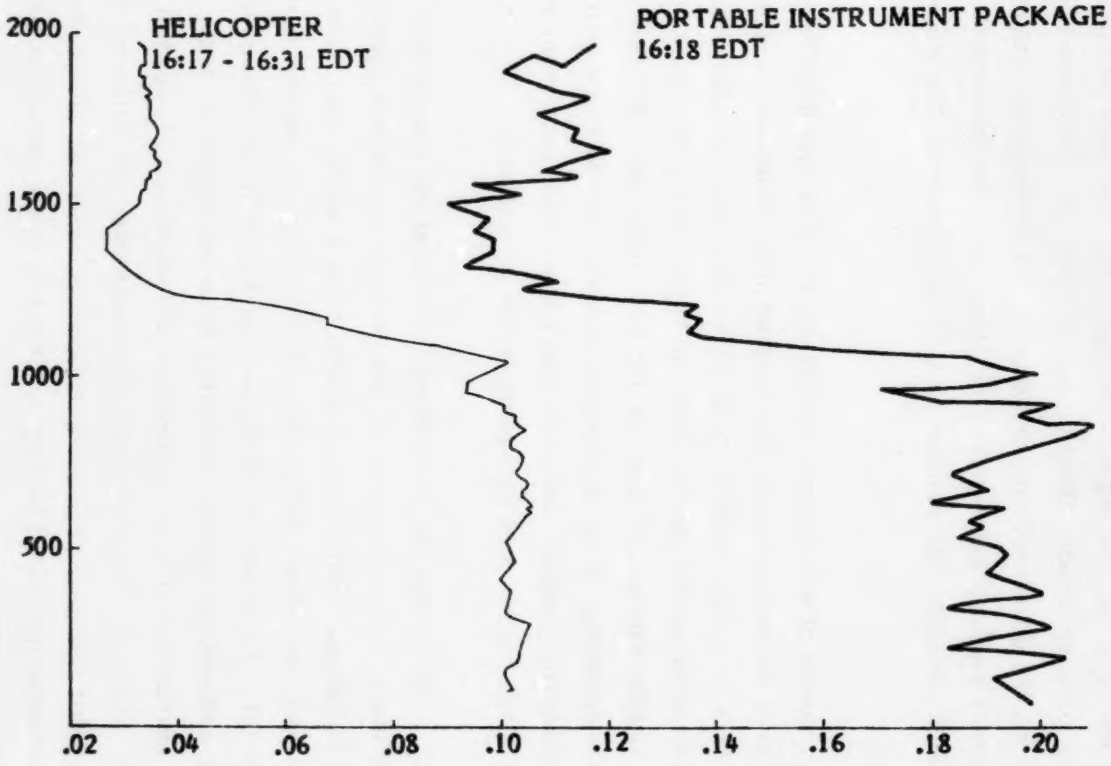

FIGURE 43. Vertical profiles of ozone obtained by the portable instrument ozone package and the instrumented helicopter on the afternoon of August 24, 1978, over Site 1.

instrument package. However, the readings from the portable instrument package are about twice those of the helicopter. The plots shown are representative of the other seven comparisons. The higher readings from the portable instrument package are apparently caused by a zero shift of the ozone instrument of that package. There is no consistent shift in the zero for the eight soundings. For the case presented, the portable instrument package reads .08 ppm higher than the instrument on the helicopter. For others, the difference may be .05 ppm. All the readings obtained with the portable instrument package are higher than those from the helicopter. Thus, there appears to be a variable, but positive zero shift throughout the side-by-side tests.

Table 22 shows results of a statistical comparison between soundings for each of the eight flights. Ozone concentrations at one-hundred meter intervals were used for the comparison. There is a very good correlation between the portable instrument package and helicopter data, except for the first two flights where the range of ozone concentrations was smaller (about .020 ppm for the first flight and 0.015 ppm for the second flight) and the clustering of all data points around a narrow range of numbers leads to a poor correlation. Analysis indicates that the portable instrument package can duplicate the helicopter if the zero shift problem can be resolved.

This zero shift problem was not discovered until after all side-by-side flights were completed and more thorough testing of the portable instrument package was done upon return to Pasadena. Those tests show that turning on the zero mode switch on the instrument does not allow adjustment of the zero; it merely turns the photomultiplier tube off. To adjust the zero, zero air has to be introduced into the analyzer by passing ambient air through activated charcoal placed in front of the sample inlet of the instrument. This ozone removal procedure was followed in flights made in September when the free lift balloon ozonesonde and tethered balloon ozonesonde systems were tested. Good agreement was achieved, as will be discussed later, between the portable instrument package and the two other techniques when the zero was properly adjusted.

The signal from the ozone instrument used in this study was fairly noisy, a consequence of the high amplifier gain settings required when Ethychem was used

Table 22. COMPARISON OF OZONE DATA (ppm) PROVIDED BY THE PORTABLE INSTRUMENT PACKAGE AND THE INSTRUMENTED HELICOPTER.

Date of Sounding	Location of Sounding	Correlation Coefficient	Range		Mean		Absolute Difference of Means	r.m.s. Difference	Number of Pairs of Data
			Package	Helicopter	Package	Helicopter			
8/18	Site 1	.58	.103 - .139	.046 - .068	.122	.057	.065	.065	19
8/18	Site 3	.51	.091 - .128	.052 - .067	.101	.060	.041	.042	18
8/19	Wilmington Airport	.94	.062 - .157	.045 - .133	.112	.095	.017	.020	21
8/22	Site 1	.74	.102 - .150	.040 - .092	.127	.068	.059	.061	18
8/22	Site 3	.88	.088 - .116	.038 - .072	.106	.058	.048	.049	17
8/23	Site 2	.84	.116 - .144	.046 - .082	.127	.066	.061	.062	16
8/23	Site 4	.94	.108 - .154	.035 - .090	.135	.069	.066	.066	19
8/24	Site 1	.98	.094 - .194	.030 - .105	.152	.072	.080	.081	19

instead of pure ethylene in the reaction cell. Thus, the profile obtained is not as smooth as that from the helicopter or the ozonesonde. If bottled ethylene were to be used, the signal-to-noise ratio would improve three-fold. However, the use of ethylene gas in an aircraft would require recertification of the plane in the "restricted" category, which defeats one of the desirable features of a portable instrument package. As noted earlier, the instrument used here does not satisfy EPA reference method designation specifications when operated with Ethychem gas.

Based on the data gathered to date, it is uncertain whether the portable instrument package can be used to measure ozone aloft, as simply as was originally hoped. Further testing of the portable instrument package is recommended.

5.4 SOUNDINGS BY OZONESONDE BENEATH A FREE LIFT BALLOON

As explained in Section 3.6, the modified ozonesonde removes SO_2 before it analyzes air samples. Also, NO_x interference is minimal. Thus, the ozonesonde measures ozone concentrations rather than total oxidants.

The modified ozonesonde also measures temperature. If a theodolite is used to track the balloon, upper air wind speed and direction can also be determined. An example of data from a sounding is shown in Figure 44. An advantage of this system over others is that it can attain higher altitudes. During the tests, the ozonesonde was easily tracked beyond 5,000 m.

Because of logistical problems, this system was not sent to the field prior to the helicopter's departure from Philadelphia. Thus, side-by-side comparison with the helicopter was not possible. However, this system was tested simultaneously with the portable instrument package and the tethered balloon ozonesonde in September.

A total of eleven soundings were made. Four of them were discarded because review of the pre-flight calibration results afterwards indicated that the response of these ozonesondes was non-linear. Two of the successful soundings were made within an hour of soundings made with the tethersonde; the portable instrument package was also flown within an hour of one of those soundings. On two other occasions, the

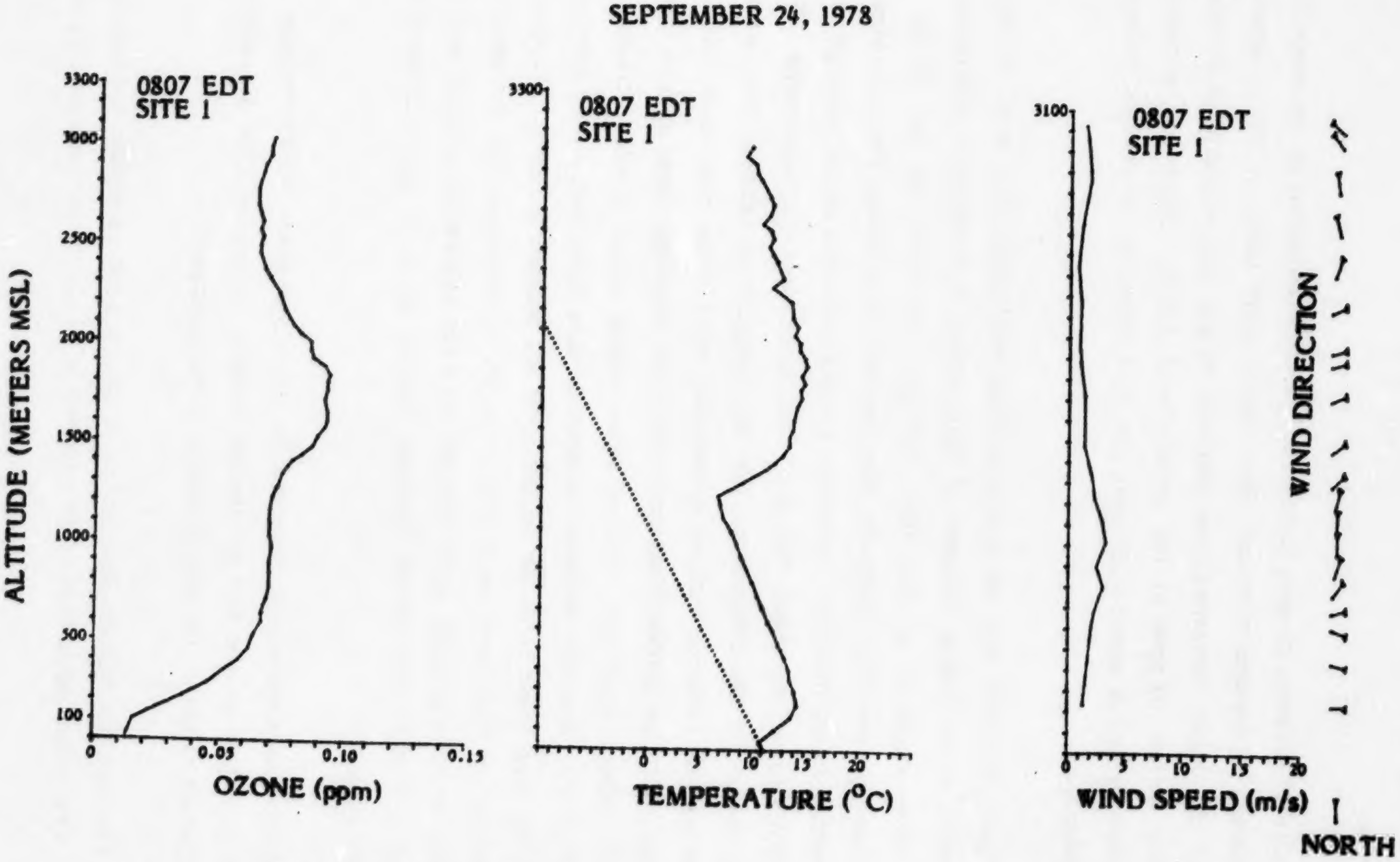

FIGURE 44. Vertical profiles of ozone, temperature, wind speed and wind direction obtained from the free lift ozonesonde sounding of 0807 EDT on September 24, 1978, over Site 1.

portable instrument package was flown within an hour of the release of the ozonesonde.

Table 23 presents ranges, means and standard deviations of the ozone concentration obtained by various methods. Data points were taken at 100 m intervals. The range of the ozone concentrations observed during each sounding is limited, usually remaining within .02 ppm of the ground-level value. Since the accuracy of the instruments tested is about ± .01 ppm, the data collected do not lend themselves well to correlations.

Figure 45 shows that the ozone profiles track each other well. If the soundings were taken within thirty minutes of each other, the absolute differences of their means were equal to or less than .010 ppm, as shown by the second and third comparisons presented in Table 23. For the first comparison, the soundings were also made within thirty minutes. However, the portable instrument package readings are consistently lower, by about .024 ppm, than those from the ozonesonde. There is no obvious reason for the difference. The two comparisons between the free lift balloon ozonesonde and tethered balloon ozonesonde were made near noon and in the late afternoon, with the tethered balloon ozonesonde soundings about an hour later than the free lift balloon soundings. Around noon, ozone values should increase with time. Consistent with this, the tethered ozonesonde data show that, on the average, readings are higher than those from the earlier free lift balloon sounding. Around 1500 EDT and thereafter, the ozone concentration begins to decrease. The tethered ozonesonde sounding, which was made later than the free lift balloon ozonesonde sounding, shows average concentrations about .020 ppm lower, which is again consistent with the assumed behavior.

Ozone concentrations observed by the ozonesonde before release are always within ± .01 ppm of the surface station reading, indicating that ozonesonde readings are accurate to within the specifications of the instrument.

The free lift balloon ozonesonde is thus a good candidate for measuring ozone aloft. One major advantage of this system is its ability to measure concentrations to

Table 23. COMPARISON OF OZONE DATA (ppm) PROVIDED BY OZONESONDE BENEATH A FREE BALLOON AND PORTABLE INSTRUMENT PACKAGE.

Technique	Date	Approximate Time (EDT)	Range		Means		Absolute Difference of Means	r.m.s. Difference	Number of Pairs of Data
			Portable Package	Ozonesonde	Portable Package	Ozonesonde			
Ozonesonde versus Portable Package	9/27	1500	.037 - .073	.063 - .088	.057	.081	.024	.025	18
	9/27	1900	.044 - .087	.046 - .073	.057	.067	.010	.015	19
	9/30	0700	.046 - .068	.032 - .057	.057	.048	.009	.012	19
			Tethered Sonde	Ozonesonde	Tethered Sonde	Ozonesonde			
Ozonesonde versus Tethered Sonde	9/27	1200	.078 - .083	.050 - .060	.082	.054	.028	.028	6
	9/27	1500	.061 - .068	.085 - .088	.066	.086	.020	.020	6

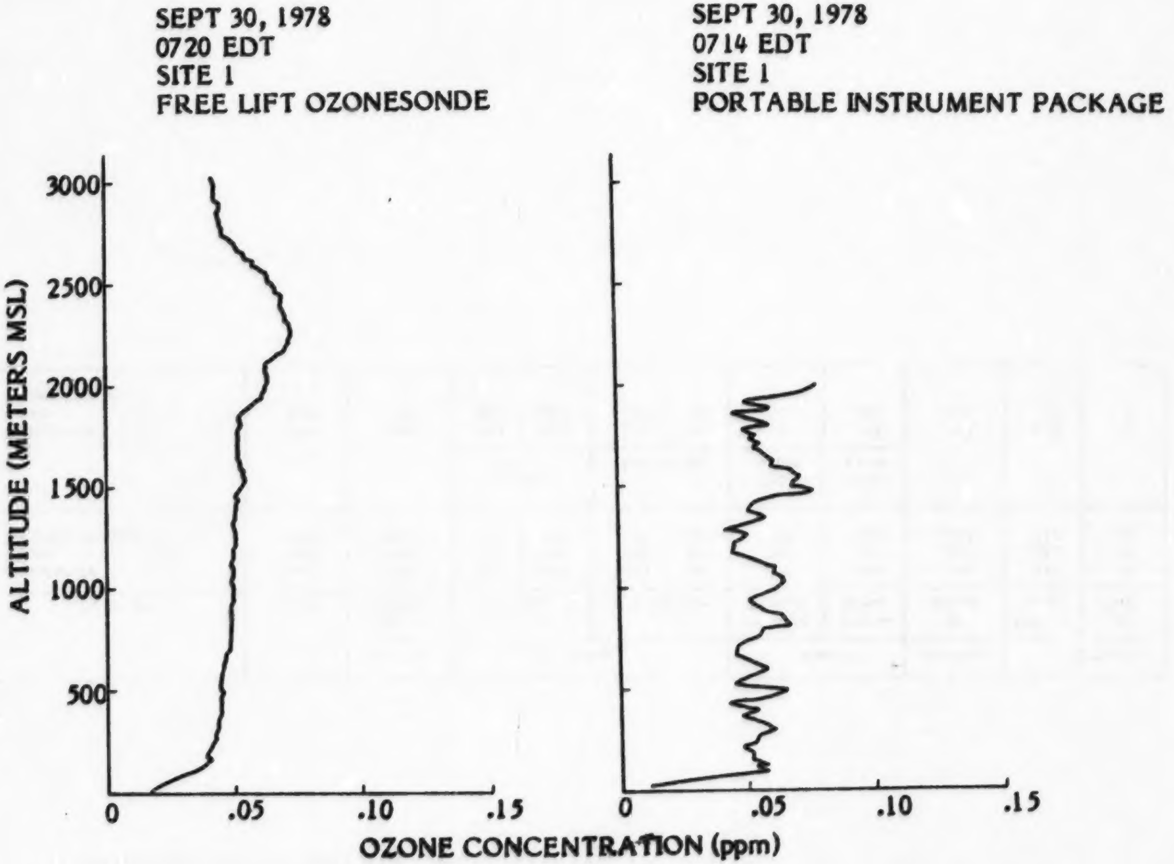

FIGURE 45. Comparison between ozone profiles taken by free lift ozonesonde and portable instrument package on September 30, 1978.

higher altitudes than all other systems considered. The disadvantage is that once it is released the system cannot be retrieved and reused.

It was learned that the calibration data should be carefully examined before launching the ozonesonde. If the instrument is determined to be non-linear it should be discarded and not launched.

5.5 SOUNDINGS BY OZONESONDE BENEATH A TETHERED BALLOON

This system is similar to the ozonesonde beneath a free lift balloon. Outputs from a tethered ozonesonde sounding are plotted in Figure 46. A comparison between this and the free lift balloon system has already been presented in the preceding section, showing good agreement between the two systems.

On August 24, a tethered ozonesonde sounding was made immediately following a sounding by the U.S. EPA helicopter. The tethered sounding was made up to 350 m AGL, while the helicopter vertical spiral ranged from 1,800 m AGL to about 100 m AGL. Thus the overlap was only about 250 m. Comparison of the data from the two systems for the 250 m indicate that measurements from the tethered ozonesonde are higher by about .045 ppm, although the trends are identical. The reason for this positive bias of the ozonesonde is unknown.

Four comparative soundings with the tethered ozonesonde and the portable instrument package were made in September. Table 24 presents the comparison results. Data used from each sounding were taken at 100 m intervals. The first two comparisons indicate that the zero shift problem of the portable instrument package was apparently not corrected at the time of the test. The later comparisons indicate that the two systems reported almost identical information.

The data show that the tethered ozonesonde accurately measures ozone concentrations aloft when the instrument is carefully calibrated. An obvious advantage of the tethered ozonesonde is that it is reusable. The major drawback (in its present configuration) could be its limited vertical range, at least with the size of balloon used here. The balloon and launch system are designed for ascent to 1,000 m above ground

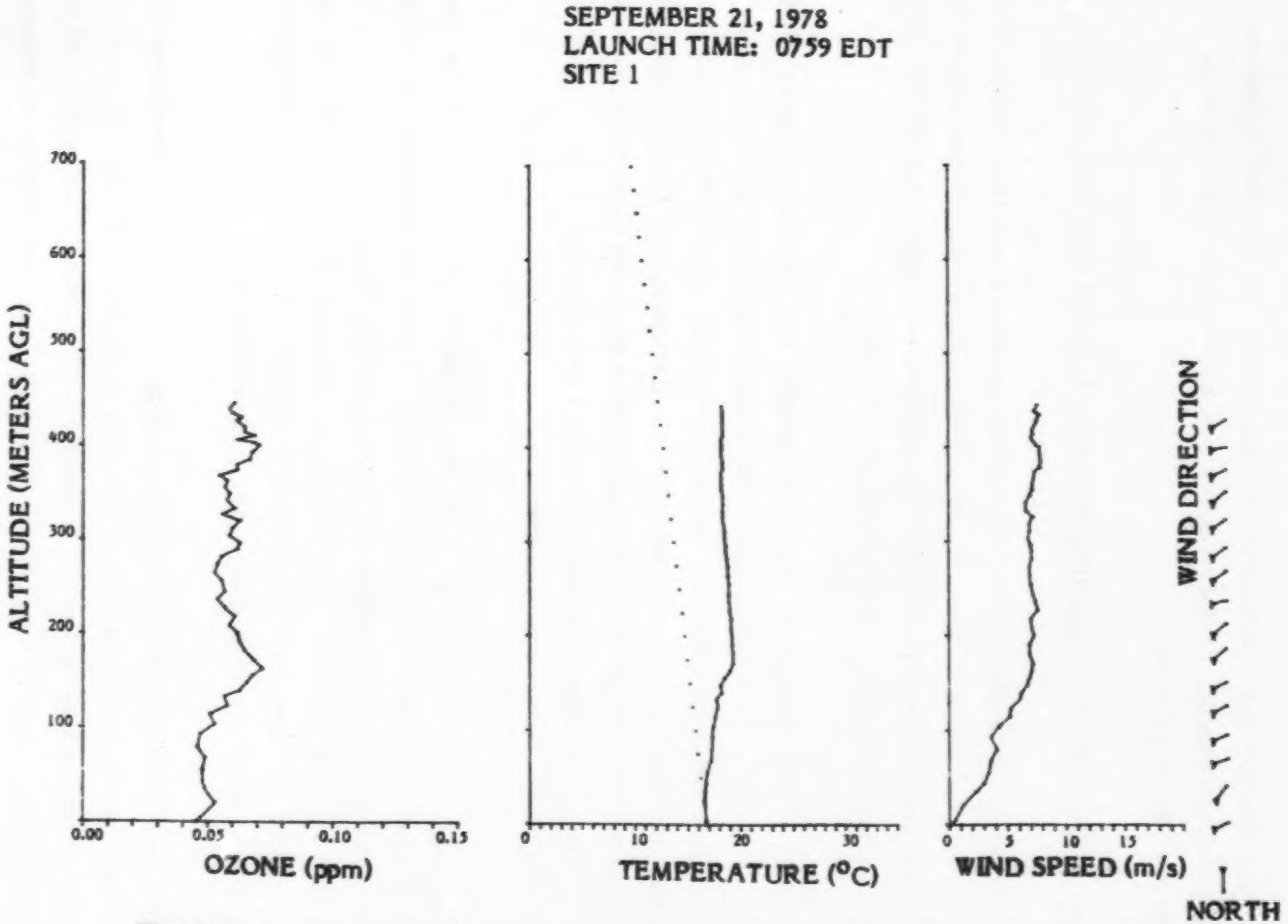

FIGURE 46. Vertical profiles of ozone, temperature, wind speed and wind direction obtained from the tethered ozonesonde sounding of September 21, 1978, beginning at 0759 EDT.

Table 24. COMPARISON OF OZONE DATA (ppm) PROVIDED BY THE OZONESONDE BENEATH A TETHERED BALLOON AND THE PORTABLE INSTRUMENT PACKAGE.

Date	Approximate Time (EDT)	Range		Means		Absolute Difference of Means	r.m.s. Difference	Number of Pairs of Data
		Portable Package	Tethered Sonde	Portable Package	Tethered Sonde			
8/24	1600	.194 - .199	.142 - .152	.196	.147	.049	.049	3
9/21	0700	.109 - .130	.034 - .066	.118	.052	.066	.066	5
9/21	1000	.059 - .084	.056 - .074	.070	.070	.000	.001	6
9/27	1600	.052 - .073	.066 - .068	.059	.067	.008	.011	5

level. As indicated by data from the other airborne techniques, the ozone structure above 1,000 m is significantly different from that in the lower 1,000 m. The tethered ozonesonde's inability to reach above this level would limit its use for measuring ozone concentrations throughout the mixing layer. A larger balloon would provide a greater altitude capability, at the expense of ease in ground handling.

6. COST EVALUATION OF SELECTED MEASUREMENT TECHNIQUES

As pointed out in Chapter 2, a fixed station costs about $40,000 to $60,000 to install and furnish with monitoring systems, and about $2,000 to $5,000 per month to operate manually. The cost of outfitting and operating an instrumented aircraft is, of course, very high. An initial investment of about $70,000 is necessary. Operating cost would be about $100 to $250 per flight hour, excluding technical labor hours required to operate the instruments onboard and reduce the data.

Thus, the costs and effectiveness of operating a portable instrument package aboard an aircraft and the ozonesonde beneath free lift and tethered balloons are of considerable interest.

Experience in utilizing the free lift ozonesonde, tethered ozonesonde, and portable instrument package during the summer of 1978 indicates that their costs would be as presented in Table 25. The initial cost includes the purchase of equipment. The operating cost includes consumable equipment and supplies for each flight. Labor hours include set-up, operation, and data reduction for each flight. The final product common to all three systems is a plot of ozone and other parameters versus altitude above ground level.

The initial cost for the free lift ozonesonde electronics package is approximately $5,000, about $4,000 more for a theodolite if wind speed and direction data were desired. Acquiring wind speed and wind direction data would also add about five labor hours to each flight. Initial costs for the tethered ozonesonde are twice as high as for the free ozonesonde due to the price of the tethered balloon and the more sophisticated sensor/transmitter which includes wind speed and wind direction. Operating costs besides labor include only the cost of helium. Labor hours are somewhat reduced since processing of the wind speed and wind direction data is automated. In addition, the labor hours per flight can be reduced if more than one flight per day is done, since set-up time for the tethersonde amounts to about two to three hours. Set-up is included in the estimate shown in Table 25.

Table 25. COST OF METHODS FOR MEASURING OZONE TRANSPORT.

Method	Parameters Measured	Initial Cost ($)	Operation Cost Per Sounding ($)	
			Labor[a]	Other
1. Free Lift Ozonesonde	Ozone, temperature, pressure Ozone, temperature, pressure, wind speed, wind direction	5,000 9,000	80 120	250 250
2. Tethered Ozonesonde	Ozonesonde, temperature, pressure, wind speed, wind direction	10,000	64	20
3. Portable Instrument Package	Ozone, temperature Ozone, NO/NO$_x$, temperature	7,500 14,500	72 96	50 50

[a] Assumed labor rate of $8 per hour.

The initial cost for the portable instrument package is $7,500 which includes the ozone analyzer, temperature sensor and recorder. Operating costs per flight (one hour) are about $50 for aircraft, pilot, and required analyzer gas. Labor time is about nine man-hours. A suitable NO/NO_x analyzer, just recently available, and recorder would increase the initial cost by about $7,000. Labor hours would increase by about two to three hours per flight if NO/NO_x analysis was performed.

Thus, the initial investment is the greatest for the tethered ozonesonde and for the portable instrument package with an NO/NO_x analyzer. Operating costs are greatest for the free lift ozonesonde, mainly because the instrument package which is lost on each flight.

Only one person is needed to operate any of the three systems and the level of technical expertise required for operation is low for all systems. The operator must have knowledge of instrument calibration, however, and all systems require access to a calibrated ozone source prior to flight.

7. RECOMMENDATIONS ON MEASUREMENT TECHNIQUES

Of the five measurement techniques evaluated, surface measurements at fixed sites, airborne measurements by dedicated instrumented aircraft, and soundings by ozonesonde beneath a free lift balloon have proven suitable for measuring directly or providing information on ozone concentrations aloft. Selection of the technique by an air pollution control agency would depend on the funding available, the intended use of the data, and the expertise of the agency. An expansion on this point will be presented later.

It is uncertain, based on the data collected thus far, whether the portable instrument package would serve the purpose of measuring the transport of ozone aloft. Since the package is easy to maintain and has lower operating costs than any of the three methods discussed earlier, it would be worthwhile to perform more tests on the system to be sure of its applicability.

The tethered balloon ozonesonde system tested here could not obtain information beyond 1000 m above ground level. Since significant ozone structures often exist above that elevation, its applicability is somewhat limited. A larger balloon would, no doubt, be able to carry the system to the desired elevation. However, the use of a larger balloon would require technicians experienced in large balloon launches and also an additional investment of about $5,000. Thus, the basic attractions of the system – ease of operation and low cost – would be diminished.

As mentioned earlier, fixed stations can be used to determine ozone aloft if it can be clearly known when mixing is complete between the surface and layers aloft. One way of obtaining that information is with an acoustic radar, which gives a continuous record of the changes of the atmospheric structure. The hourly average concentration immediately following the mixing is found to be most representative of the concentration aloft. The use of an acoustic radar, along with a surface monitoring station upwind of an urban area, would be a practical approach for quantifying transport into an urban area. This combination would provide continuous information for purposes of routine surveillance and input to models. This approach is within the technical capability of all air pollution control agencies currently maintaining air quality monitoring stations. Initial cost of such a station (with an acoustic radar) would be about $40,000 to $70,000 and the operating cost would be about $2,000 to $5,000 per month.

A dedicated instrumented aircraft is the best airborne measurement platform. However, the approach is probably beyond the financial and technical means of many local and state air pollution control agencies. Also, it is not practical for routine surveillance. It is, however, the best approach to quantify ozone levels aloft on days that are forecast to have significant transport and/or high ground-level ozone concentrations. Thus, this is a recommended approach for obtaining inputs to models and special research studies for agencies that can either afford to instrument an aircraft or hire consultants that can provide instrumented aircraft.

The free lift balloon ozonesonde system is one that most air pollution control agencies would no doubt be able to afford and have the technical capability to operate. Similar to the dedicated instrumented aircraft, this approach would not be practical for routine surveillance. It would be an appropriate technique to measure ozone concentrations aloft for input into models and for studying vertical ozone distributions during ozone episodes.

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APPENDIX A

The results of the first (July 18-26, 1978), second (July 31-August 4, 1978), and third (September 5-9, 1978) audits of the Northeast Oxidant Transport Study are contained in Tables A-1, A-2, and A-3. Table A-1 contains the nitrogen oxides audit data, Table A-2 contains the ozone audit data, and Table A-3 contains the meteorological audit data for the network as a whole. The AeroVironment hydrocarbon analyzers were only audited during the third period. Audit results are given in Table A-4.

Table A-1. Summary of the Northeast Oxidant Transport Study Nitrogen Oxides Audit Results.

Station Location Affiliated Organization	Nitrogen Oxides Analyzer - Regression of Analyzer Response on Audit Concentration								
	NO Channel[a]			NO_2 Channel[a]			NO_x Channel[a]		
	1st Audit	2nd Audit	3rd Audit	1st Audit	2nd Audit	3rd Audit	1st Audit	2nd Audit	3rd Audit
Lancaster, Pennsylvania State of Pennsylvania	NR	NA	NR	0.8169 0.044	NA	NO	NR	NA	NR
Broad and Spruce City of Philadelphia	0.9578 0.003	NA	1.0536 -0.001	0.9930 -0.001	NA	0.9916 -0.017	0.9591 0.002	NA	NR
Franklin Institute City of Philadelphia	1.0941 -0.019	NA	NO	1.0968 0.017	NA	NO	1.1165 -0.025	NA	NO
Hockessin, Delaware AeroVironment	1.0657 -0.015	1.0070 -0.002	1.0861 -0.012	0.9439 -0.008	0.9964 0.000	1.0270 -0.009	1.0662 -0.015	1.0080 -0.004	1.0640 -0.011
Downingtown, Pennsylvania AeroVironment	1.0124 -0.004	1.0725 -0.009	1.0410 0.001	0.9252 0.003	1.0523 0.003	1.0480 -0.008	1.0012 -0.003	1.0586 -0.008	1.0320 -0.002
Collegeville, Pennsylvania AeroVironment	1.0611 0.028	1.0037 -0.004	1.0340 0.004	0.9760 0.013	1.0768 -0.011	1.0430 -0.011	NO	0.9948 -0.008	0.9980 0.009
Woodstown, New Jersey AeroVironment	0.9647 0.016	1.0818 0.009	1.0213 -0.006	0.9616 0.023	1.0848 -0.004	1.0161 0.004	0.9730 0.009	1.0686 0.007	1.0228 -0.006
Ringoes, New Jersey AeroVironment	NO	NO	1.0000 -0.068	NO	NO	0.9813 0.000	NO	NO	0.9929 -0.083
EMSL Helicopter Wilmington, Delaware	NA	1.1950 -0.007	NA	NA	NR	NA	NA	1.2160 -0.010	NA

NA - Not audited
NR - Not recorded
NO - Not operational
[a] Regression indices calculated from the audit data and presented as follows: [Regression Slope]

Table A-2. Summary of the Northeast Oxidant Transport Study Ozone Audit Results

Station Location / Affiliated Organization	Ozone Analyzer - Regression of Analyzer Response on Audit Concentration					
	1st Audit		2nd Audit		3rd Audit	
	Slope	Intercept	Slope	Intercept	Slope	Intercept
Lancaster, Pennsylvania	1.3593	0.109	NA	NA	0.8640	0.005
State of Pennsylvania						
Somerville, New Jersey	0.9874	-0.004	NA	NA	NO	NO
Ancora, New Jersey	0.9618	0.015	NA	NA	NO	NO
Bivalve, New Jersey	0.6419	0.004	NA	NA	0.9301	0.002
State of New Jersey						
Broad and Spruce	0.9143	0.000	NA	NA	0.9273	0.009
Franklin Institute	0.9842	0.003	NA	NA	1.0193	-0.008
City of Philadelphia						
Hockessin, Delaware	0.8951	-0.012	0.8834	0.004	0.9328	0.009
Downingtown, Pennsylvania	0.7790	0.004	0.7857	0.002	1.0007	0.001
Collegeville, Pennsylvania	0.9320	-0.001	0.6826	-0.004	1.1374	0.002
Woodstown, New Jersey	1.0547	0.024	0.7798	0.001	0.8665	-0.001
Ringoes, New Jersey	0.8247	0.051	NO	NO	1.1380	0.010
Aircraft	NA	NA	NA	NA	0.8875	0.009
AeroVironment						
EMSL Helicopter	NA	NA	1.0392	-0.002	NA	NA
Wilmington, Delaware						

NA - Not audited

NO - Not operational

Table A-3. Summary of the Northeast Oxidant Transport Study Meteorological Audit Results.

Station Location Affiliated Organization	1st Audit				2nd Audit				3rd Audit			
	WS	WD	T	DP/RH	WS	WD	T	DP/RH	WS	WD	T	DP/RH
Lancaster, Pennsylvania State of Pennsylvania	O	O	O	O	NA	NA	NA	NA	NO	NO	NO	NO
Somerville, New Jersey Ancora, New Jersey Bivalve, New Jersey State of New Jersey	NI NI NO	NI NI NO	NI NI NI	NI NI NI	NA NA NA	NA NA NA	NA NA NA	NA NA NA	NR NR O	NR NR O	NR NR NR	NI NI NI
Broad and Spruce Franklin Institute City of Philadelphia	NO NI	NO NI	NI O	NI NI	NA NA	NA NA	NA NA	NA NA	NO NI	NO NI	NR O	NI NI
Hockessin, Delaware Downingtown, Pennsylvania Collegeville, Pennsylvania Woodstown, New Jersey Ringoes, New Jersey AeroVironment	NI O O NI NI	NI O O NI NI	NI NI O NI NI	NI NI NI NI NI	O NO O O O	NO O O NO O	NR NR O O NR	NR NR NR NR NR	O O NO IO O	O O NO O O	NR NR NO O NR	NI NI NI NI NI

NA - Not audited
O - Sensor operational
NO - Sensor not operational
NI - Sensor not installed at station
NR - Index not recorded at station
WS - Wind speed
WD - Wind direction
T - Temperature
DP/RH - Dew point/relative humidity

Table A-4. REGRESSION ANALYSIS OF BECKMAN 6800 GAS CHROMATOGRAPH RESPONSE ON AUDIT CONCENTRATION.

Station Location Affiliated Organization	THC Channel			Methane Channel		
	m	b	r	m	b	r
Hockessin, DE	0.9672	0.021	0.9999	0.9581	-0.063	0.9999
Downington, PA	0.9066	-0.219	0.9943	0.7442	-0.028	0.9991
Collegeville, PA	0.8403	0.155	0.9869	0.9987	-0.210	0.9992
Woodstown, NJ	0.8900	-0.094	0.9995	0.8693	0.072	0.9999
Ringoes, NJ	0.9312	0.331	0.9982	0.5193	0.342	0.9984
AeroVironment						

m - Regression slope

b - Regression intercept

r - Regression correlation coefficient